PB85-234672

Investigation of Polycyclic Aromatic Hydrocarbon Discharges to Water in the Vicinity of Buffalo, New York

New York State Dept. of Environmental
Conservation, Albany

Prepared for

Environmental Protection Agency, Chicago, IL

Feb 85

U.S. Department of Commerce
National Technical Information Service
NTIS

United States
Environmental Protection
Agency

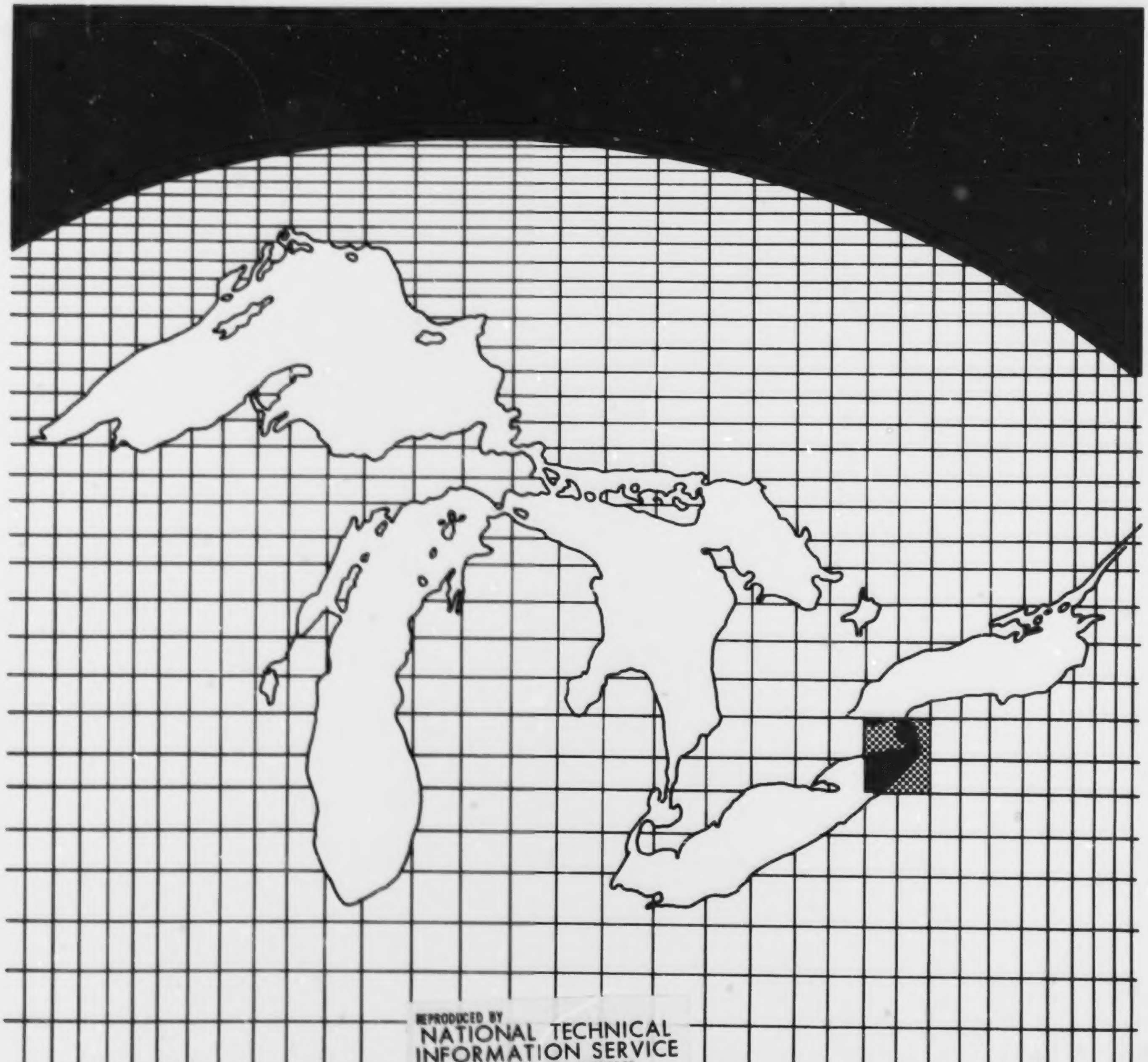
Great Lakes National
Program Office
536 South Clark Street
Chicago, Illinois 606005

EPA-905/4-85-002
February 1985

PB85-234672

B292 / 197

Investigation of Polycyclic Aromatic Hydrocarbon Discharges To Water in the Vicinity Of Buffalo, New York



REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

THIS FORM IS PRINTED AS THE FINAL PAGE IN THE ATTACHED REPORT

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-905/4-85-002

2.

3. RECIPIENT'S ACCESSION NO.
PB85 234672 /AS

4. TITLE AND SUBTITLE
Investigation of Polycyclic Aromatic Hydrocarbon Discharges to Water in the Vicinity of Buffalo New York

5. REPORT DATE
February 1985

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
Edward J. Kuzia and John J. Black

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
New York State Department of Environmental Conservation
50 Wolf Road
Albany, New York 12233

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
R00556610-01

12. SPONSORING AGENCY NAME AND ADDRESS
U.S.Environmental Protection Agency
Great Lakes National Program Office
Chicago, Illinois 60605

13. TYPE OF REPORT AND PERIOD COVERED
Final

14. SPONSORING AGENCY CODE
Great Lakes National Program Office
USEPA, Region V

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Eastern Lake Erie and the upper Niagara River basin were sampled for polycyclic aromatic hydrocarbons (PAH) to assess their distribution and sources. Twenty-five sites were sampled using polypropylene substrates. Five areas were identified as having relatively high PAH contamination. These were Lake Erie at the mouth of Smoke Creek, the Union and Lackawanna Ship Canals, the Buffalo River, Two Mile Creek, and the Buffalo Sewer Authority. Subsequent sampling and analyses of sediments, water, and polypropylene substrates confirmed the preliminary findings. The sources of the PAH were attributed to steel manufacturing operations (Lake Erie at the mouth of Smoke Creek and Union and Lackawanna Ship Canals) and oil storage facilities (Two Mile Creek). The Buffalo Sewer Authority was sampled directly in the outfall, and the analytical results identified it as a source of PAH to the Niagara River. The Buffalo River had several PAH inputs near the South Park Bridge. In addition to the areas identified as having high PAH contamination, there was a generalize PAH contamination throughout the study area.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Polycyclic Aromatic Hydrocarbons Contaminants Sediments Waters		

18. DISTRIBUTION STATEMENT
Document is available to the public through the National Technical Information Service
Springfield, Virginia 22151

19. SECURITY CLASS (This Report)
Unclassified

20. SECURITY CLASS (This page)
Unclassified

21. NO. OF PAGES
144

22. PRICE

EPA Form 2220-1 (9-73)

☆ U.S. GOVERNMENT PRINTING OFFICE: 1985—555-755/549

EPA-905/4-85-002
February 1985

INVESTIGATION OF POLYCYCLIC AROMATIC HYDROCARBON DISCHARGES TO WATER IN THE VICINITY OF BUFFALO, NEW YORK

By

Edward J. Kuzia
New York State
Department of Environnmental Conservation
Albany, New York 12233

and

John J. Black
New York State
Department of Health
Roswell Park Memorial Institute
Buffalo, New York

Grant No. R00556610-01

Projector Officer

Vacys J. Saulys
Great Lakes National Program Office
United States Environmental Protection Agency
536 South Clark Street
Chicago, Illinois 60605

DISCLAIMER

This report has been reviewed by the Great Lakes National Program Office, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commericial products constitute endorsement or recommendation for use.

FOREWORD

The Great Lakes National Program Office (GLNPO) of the United States Environmental Protection Agency was established in Region V, Chicago, to focus attention on the significant and complex natural resources represented by the Great Lakes.

GLNPO implements a multi-media environmental management program drawing on a wide range of expertise represented by universities, private firms, State, Federal, and Canadian governmental agencies, and the International Joint Commission. The goal of the GLNPO program is to develop programs, practices and technology necessary for a better understanding of the Great Lakes Basin ecosystem, and to eliminate or reduce to the maximum extent practicable the discharge of pollutants into the Great Lakes system. GLNPO also coordinates U.S. actions in fulfillment of the Agreement between Canada and the United States of America on Great Lakes Water Quality of 1978.

This investigation was funded in partial support of the binational study of the Niagara River toxic contaminant problems.

TABLE OF CONTENTS

Page

- ABSTRACT vi
- LIST OF FIGURES vii
- LIST OF TABLES viii
- INTRODUCTION 1
- MATERIALS AND METHODS 3
  - ANALYTICAL METHODS 3
    - Solvents and Standards 3
    - Polypropylene Substrates 3
    - Sediments 6
    - Aqueous Samples 7
  - QUANTITATIVE HPLC ANALYSES FOR SEDIMENTS AND AQUEOUS SAMPLES 8
  - FIELD SAMPLING 11
  - STATISTICAL TREATMENT 11
- RESULTS AND DISCUSSION 13
  - PRELIMINARY SURVEY 13
  - VERIFICATION SAMPLING 17
    - Buffalo Sewer Authority 28
    - Buffalo River 28
    - Smoke Creek and Union and Lackawanna Canals 37
    - Two Mile Creek 43
  - COMPARISION OF PAH TYPES AMONG SITES 52
- CONCLUSIONS 54
- RECOMMENDATIONS 56
- LITERATURE CITED 57

APPENDIX

A. PAH CHROMATOGRAMS OF ARTIFICIAL SUBSTRATE
SAMPLING OF PRELIMINARY SURVEY SITES.................... 59

B. PAH SEDIMENT CONCENTRATIONS.............................. 67

C. SITE DESCRIPTIONS.. 98

D. QUALITY CONTROL MEASURES................................. 103

ABSTRACT

Eastern Lake Erie and the upper Niagara River basin were sampled for polycyclic aromatic hydrocarbons (PAH) to assess their distribution and sources. Twenty-five sites were sampled using polypropylene substrates. Five areas were identified as having relatively high PAH contamination. These were Lake Erie at the mouth of Smoke Creek, the Union and Lackawanna Ship Canals, the Buffalo River, Two Mile Creek, and the Buffalo Sewer Authority. Subsequent sampling and analyses of sediments, water, and polypropylene substrates confirmed the preliminary findings. The sources of the PAH were attributed to steel manufacturing operations (Lake Erie at the mouth of Smoke Creek and Union and Lackawanna Ship Canals) and oil storage facilities (Two Mile Creek). The Buffalo Sewer Authority was sampled directly in the outfall, and the analytical results identified it as a source of PAH to the Niagara River. The Buffalo River had several PAH inputs near the South Park Bridge. In addition to the areas identified as having high PAH contamination, there was a generalized PAH contamination throughout the study area.

LIST OF FIGURES

Page

Fig. 1* Preliminary Artificial Substrate Sampling Sites and Relative Total PAH Concentration............ 14

Fig. 2* PAH Sediment Sampling Sites. Buffalo River with Relative Total PAH Concentration................ 18

Fig. 3* PAH Sediment Sampling Sites. Smoke Creek Transect in Lake Erie with Relative Total PAH Concentration.................................. 19

Fig. 4* PAH Sediment Samling Sites at Union and Lackawanna Canals with Relative PAH Concentration.. 20

Fig. 5* PAH Sediment Sampling Sites at Two Mile Creek with Relative PAH Concentration....................... 21

Fig. 6* Total PAH Sediment Concentrations and Corresponding Artificial Substrate Total PAH Group for Similar Stations... 27

Fig. 7* Artificial Substrate Sampling Sites in Buffalo River.. 31

Fig. 8 Buffalo River Artificial Substrate Sampling Sites Near South Park Bridge and Total PAH................. 34

Fig. 9 Percent Composition of Total PAH Compounds in Sediment at Buffalo River Sites 5 and 6............... 36

Fig. 10* Artificial Substrate Sampling Sites at Smoke Creek and the Union and Lackawanna Canals.................. 38

Fig. 11* Cluster Map of Association of Sediment Sampling Sites Based on Their PAH Composition................. 41

Fig. 12* Two Mile Creek Artificial Substrate Sampling Sites.... 44

Fig. 13 Percent Composition of Total PAH in Two Mile Creek Artificial Substrate Sites.......................... 49

Fig. 14 Percent Composition of Total PAH Compounds in Sediment.. 51

* Detailed site description for these figures are presented in Appendix C

LIST OF TABLES

		Page
Table 1	PAH Screening Results	15
Table 2	PAH Concentrations in Water Samples from Smoke Creek, Bethlehem Steel Outfalls to Smoke Creek and the Lackawannna Sewage Treatment Plant	23
Table 3	PAH Concentrations in Water from Buffalo Color Water Outfalls and Intake	24
Table 4	PAH Concentrations in Water from Allied Chemical Outfalls to Buffalo River	25
Table 5	PAH Concentrations in Buffalo Sewer Authority Outfall Water	26
Table 6	PAH Concentration Artificial Substrates from Buffalo River	29
Table 7	PAH Sediment Concentrations at Buffalo River Sites 5 and 6	33
Table 8	PAH Concentrations in Artificial Substrates Smoke Creek and Union and Lackawanna Canals	39
Table 9	PAH Percent Composition of Clusters from Cluster Map of Site Association	42
Table 10	PAH Concentrations in Artificial Substrates from Two Mile Creek	45
Table 11	PAH Sediment Concentration from Two Mile Creek	47

INTRODUCTION

INTRODUCTION

Anthropogenic polynuclear aromatic hydrocarbons (PAH) are contaminants of aquatic ecosystems. These compounds have been reported in fish (Neff, 1982), invertebrates (Eadie et al, 1982), sediment (Heit et al., 1981), and water (Basu and Saxena, 1978). PAH can enter the aquatic environment from various sources, which include airborne deposition into water from anthropogenic and natural combustion processes (Hert et al., 1981), runoff from urban areas and roadways (Wong, 1981), and municipal or industrial effluents (Baum, 1978). Because incomplete combustion of organic material can result in PAH production, in particular combustion of fossil fuels, there is a potential for eventual dispersal of these compounds throughout aquatic ecosystems.

The potential for pollution of the aquatic ecosystem with these compounds presents a significant problem due to the potent carcinogenicity of compounds such as dibenzanthracene and benzo(a)pyrene. PAH produce skin tumors in mice and have been associated with occupational cancers (USEPA, 1980). Black (1983) has demonstrated a relationship between tumors in fish and PAH contaminated sediments. Therefore, these compounds are not only carcinogens of humans, but may also produce cancers in feral fish.

The study described here had three major objectives: 1) development of source identification techniques for PAH in ambient waters, 2) localization of sources of PAH in eastern Lake Erie and the Upper Niagara River, and 3) determination of the distribution, type, and concentrations of PAH in eastern Lake Erie and the upper Niagara River. The development of source identification techniques centered around the use of an artificial substrate which is the same material used for containing oil spills (3 M Brand Oil Sorbent Type 151). In addition to development of artificial substrates, conventional media (water and sediment) were also analyzed for PAH. These analyses not only identified the distribution and relative contamination with PAH in the study area, but, they also were used to assist in source identification and the evaluation of the artificial substrate as a PAH monitoring tool.

The general strategy employed to identify PAH sources was deployment of artificial substrates throughout the area under study. Sites for the preliminary survey were selected by staff from the New York State Department of Environmental Conservation (DEC) and the contractor. Sites were also selected where PAH input was not suspected. Results of this preliminary survey were reviewed by the same group and subsequent sampling was designed to verify inputs of PAH where high levels were identified in the preliminary sampling. Analyses of water and sediment were also done to confirm the results of artificial substrate sampling.

MATERIALS AND METHODS

ANALYTICAL METHODS

Solvents and Standards

All solvents were redistilled in glass from technical grade solvents using a reflux-type condenser (Fisher Scientific #07-748). Acetonitrile (Fisher Scientific, pesticide grade) and dimethyl sulfoxide (Me_2SO) were used without further purification.

Potassium hydroxide and sodium sulfate were reagent grade (Fisher Scientific). Florisil (J.T. Baker, 60-100 mesh) was washed to remove fines and then activated by heating overnight to 180 °C and after cooling, partially deactivated by addition of 2.5% distilled water by weight of Florisil.

PAH standards were obtained from Supelco, PAH mixture 610-M, and as Standard Reference Material #1647 (National Bureau of Standards). 2-methylphenanthrene, 2-methylanthracene, and perylene were supplied by Dr. Fred Block, Roswell Park Memorial Institute, Buffalo, N.Y.

Polypropylene Substrates

Polypropylene substrates measuring 5.0 cm x 10.0 cm were cut from sheets of a commercially available oil-absorbent cloth (3M Brand Oil Sorbent Type 151). Substrates were wrapped in foil to avoid contamination prior to use. The buoyant artificial substrates were attached to an anchored wooden float by a short nylon line and allowed to trail freely in the current. Spring-loaded metal clips facilitated rapid substrate installation and removal under field conditions. After exposure periods of 96 h, substrates were removed, immediately wrapped in foil, and returned to the laboratory where they were stored at -10 °C prior to extraction and analysis.

Substrates were placed in 43 mm x 123 mm cellulose thimbles (Whatman) and extracted with 95% ethanol in a Soxhlet apparatus for 4 h (approximately 16 cycles). The ethanol extract (250 ml) was transferred to a separatory funnel containing 230 ml of water and 250 ml of cyclohexane, and a nonpolar fraction was isolated by liquid-liquid partitioning. After solvent exchange of the cyclohexane for dimethyl sulfoxide (Me_2SO), a PAH-containing fraction was isolated by Me_2SO partitioning and back-extraction procedures as those utilized by Dunn (1979) for isolation of PAH from marine organisms.

Following Dunn, the solvent exchanged Me_2SO was transferred along with a 5ml Me_2SO rinse from the evaporation flask to a separatory funnel containing 10 ml of hexane. After vigorous shaking, the Me_2SO hypophase was transferred to a second separatory funnel. The hexane phase in the first funnel was extracted a second time with a fresh 10 ml volume of Me_2SO, and this was also added to the second separatory funnel. Following addition of 40 ml of water and 20 ml of cyclohexane to the second funnel, the PAH was back-extracted into the cyclohexane. The aqueous Me_2SO phase was drained into a third funnel and extracted again with 20 ml of cyclohexane. The two cyclohexane phases were combined and washed with distilled water.

This fraction, containing the bulk of the PAH, was reduced in volume to approximately 3 ml and transferred to a conical tube where the hydrocarbons contained in the fraction were concentrated into an accurately measured volume of Me_2SO (0.5-1 ml) by evaporating off the cyclohexane. The resulting analytical fractions were transferred to septum-covered injection vials (Varian Associates) and stored in the dark prior to analysis.

The PAH content of artificial substrate derived analytical fractions was characterized using reverse phase gradient elution HPLC. Analyses were performed on a Perkin-Elmer Series 3 Liquid Chromatograph using acetonitrile and water as the elution solvent system. In characterizations of some initial samples, an in-house repacked column (2.1 mm i.d. x 250 mm, Vydac TP201, 10 uM ODS packing material) was employed. All other samples were analyzed using a commercially available column (Perkin-Elmer HC-ODS). Chromatographic conditions were varied to accomodate column characteristics. Eluted compounds were detected by UV absorbance (254 nM) using a Perkin-Elmer LC-15 fixed wavelength detector. Peak identifications were assigned on the basis of retentions relative to an internal reference compound (chrysene) and by trace enrichment with a mixture of PAH standards.

Gradient programs:

In house repacked column: TP201, 10 uM ODS, flow 0.6 ml/min
T_1 - isocratic, 2.5 min, 55% acetonitrile/H_2O
T_2 - 25 min linear to 99.9%, 55% acetonitrile/H_2O
T_3 - 20 min hold at " , " " "
T purge - 5 min, 99.9%, " " ", flow rate 2.0 mls/min
T equilibrate - 20 min 55% acetonitrile/H_2O, flow rate 0.6 ml/min

Perkin-Elmer SIL HC-ODS, flow 0.9 ml/min

T_1 - isocratic, 1.5 min, 55% acetonitrile/H_2O

T_2 - 15 min liner to 99.9% acetonitrile/H_2O

T_3 - 10 min hold at " " "

T purge - 5 min 99.9% acetonitrile/H_2O, flow rate 2.0 ml/min

T equilibrate - 15 min, 55% acetonitrile/H_2O, flow rate 0.9 ml/min

Sediments

To compensate for variable sediment composition, concentrations were expressed in terms of wet weight, dry weight, and the weight of organic matter in the sample. Paired sub-samples were used with one taken through extraction and analysis and the other dried to constant weight at 60°C followed by combustion at 500°C for 24 hours. The organic weight was the loss in weight between 60°C and 500°C.

Methods of sample extraction and PAH prefractionation were similar to those employed by Dunn (1979). Samples of wet sediment (2-20 gms) were digested in boiling ethanol/potassium hydroxide by liquid-liquid extraction. The cyclohexane phase was concentrated and a PAH containing fraction isolated by chromatography on Florisil.

A 22 x 400 mm column was dry-packed with 25 gms of partially deactivated (2.5% wt/vol) 60-100 mesh Florisil topped with 20 gms of sodium sulfate. Following a hexane prewash, the cyclohexane phase was percolated into the column. This fraction, contaminated with aliphatics, was discarded. The PAH fraction was eluted from the column with three 50 ml washes of 50% methylene chloride/hexane. This fraction was concentrated into 5 ml of Me_2SO by flash evaporation.

Additional aliphatics were removed by partitioning of the PAH between Me_2SO and hexane. After adding water, the aromatic hydrocarbons were back extracted from the Me_2SO into a fresh volume of cyclohexane. The PAH were concentrated into an accurately measured volume of Me_2SO by evaporating off the cyclohexane using a gentle stream of warm air. Aliquots of from 1 to 20 ul were injected for HPLC analysis.

Aqueous Samples

A simple "trapping" technique was applied to aqueous samples. Aqueous effluents were sampled by vacuum aspiration (1500 - 1800 mls) through a commercial reversed phase cartridge, J.T. Baker, 6.0 ml reversed phase, octyl and octadecyl, extraction columns. To prevent cartridges from rapid plugging by coarse particulates, a small amount of glass wool was placed in the cartridge. Following collection of the sample, the column was eluted with a 10 ml volume of 90% acetonitrile/10% methanol. A simple liquid-liquid partitioning scheme was employed for sample clean up. Following elution of the extraction columns/cartridge, 20 mls of distilled water and 10 mls of hexane were added to the 10 ml sample in 90% acetonitrile/10% methanol in a 125 ml separatory funnel. This aqueous solution was extracted by the hexane. The aqueous phase was discarded and the hydrocarbon solvent was reduced in volume to approximately 1 ml in a conical 2 ml test tube. A carefully measured volume (usually 50 ul) of Me_2SO was added to the PAH containing fraction and the remaining hexane removed by evaportation under a gentle stream of warm air. Samples of 1- 10 ul were injected into the HPLC for analysis of PAH. This procedure assures only a semi-quantitative result due to low recoveries. Average PAH recoveries ranged from 25% for the octadecyl cartridge to 50% for the octyl cartridge.

QUANTITATIVE HPLC ANALYSES FOR SEDIMENTS AND AQUEOUS SAMPLES

The PAH content of analytical fractions was estimated by using reverse phase gradient elution HPLC. Analyses were performed using a Perkin-Elmer series 3B liquid chromatograph and acetonitrile/water as the eluting solvent system. Although solvent gradients were varied to accommodate column characteristics, flow rates of 1.0 to 1.5 mls/min and linear solvent gradients from 40% to 100% (15 to 40 minutes in length depending on column characteristics) gave satisfactory results.

Although several commercial brands of PAH selective columns were employed (Supelco, Supelcosil LC-PAH; Perkin-Elmer PAH_{10}; and Vydac 201TP 54.6), most samples were analyzed on the Vydac column. In the absence of interfering compounds, all three brands were capable of completely resolving all 16 EPA priority PAH. At the first signs of loss of column resolution or selectivity, the column was either reversed or replaced to restore the effectiveness of the separation.

The column was connected in series to an absorbance detector (Perkin-Elmer LC-75 spectrophotometer equipped with an autocontrol for scanning of spectra) and a fluorescence detector (Perkin-Elmer 650-10S fluorospectrophotometer equipped with a by-pass valve enabling the flow cell to be taken offline for spectral scanning). In this arrangement, low molecular weight PAH compounds were detected by their absorbance at 254 nM and higher molecular weight PAH compounds were detected by their fluorescence signals. An exciting wavelength of 295 nM and an emission wavelength of 405 nM, using a slit width of 10 nM (both excitation and emission monochrometers) were used.

Absorbance data were quantified using a Spectra-Physics 4100 computing integrator. Peaks detected by their fluorescence were quantitated using a Hewlett-Packard 3390A integrator. All PAH compounds were quantitated on the basis of peak areas and individual response factors.

Gradient program

Column: Vydac 201TP 54.6, C_{18}; flow rate 1.5 ml/min; initial solvent 40% acetonitrile/H_2O

T_1 - 40 min linear to 99.9% acetonitrile/H_2O

T_2 - 22 min hold at " " "

T_3 - 2.5 min linear return to 50% acetonitrile/H_2O

T equilibrate - 10 min at 40% acetonitrile/H_2O

Although all components present in PAH containing analytical fractions were not identified, 16 components were identified as PAH compounds. Peaks were identified on the basis of relative retention times and co-chromatography with available PAH standards. Internal reference peaks used were phenanthrene and chrysene(absorbance chromatograms) and benzanthracene, benzo(k)fluoranthene, and 3,4-benzo(a)pyrene (fluorescence chromatograms). Chrysene was added as an internal reference compound by co-injecting a volume equal to 25 ng along with the sample. In addition, seven compounds were confirmed (in selected samples) on the basis of spectral characteristics identifiable to the compound of interest. Although compounds were not routinely confirmed spectroscopically, most sediment samples exhibited similar peak distributions characteristic of a PAH "fingerprint". The compounds carbazol, naphthylene, acenaphthylene, and acenaphthene may have been present in most samples. The volatility and solubility characteristics of these compounds interfered with their quantitative recovery in the Florisil chromatography and clean up procedures.

The following compounds usually appear to be well resolved by the chromatographic conditions employed: phenanthrene, anthracene, benzanthracene, chrysene, benzo(k)fluoranthene, and benzo(a)pyrene. Mesurements of these PAH (in the samples analyzed for the present project) usually reflect a high degree of accuracy. Other PAH, including fluoranthene, methylphenanthrene, pyrene, methylanthracene, and benzofluorene, were variably resolved from neighboring peaks and therefore data for these compounds reflect a lower degree of accuracy. Data for these PAH should be useful for comparison purposes within the study areas as well as providing semi-quantitative data for external comparison. Two compounds, dibenz(a,h)anthracene and benzo(g,h,i)perylene, although potentially well resolved by the fluorescence detection method, are generally present at only trace levels (relative to the amounts of other PAH) and the routine measurements of these two PAH may exhibit a variable degree of certainty depending upon the concentrations of these compunds relative to fluorescence background materials in the high molecular PAH region of the chromatogram. Two more compounds, perylene and benzo(b)fluoranthene, appear to co-elute. In this situation the peak(s) is quantitated as perylene by UV absorbaance and as benzo(b)fluoranthene by fluorescence. Thus, data represent maximal estimates for these two compounds.

FIELD SAMPLING

Polypropylene substrates were used exclusively in a preliminary sampling survey which was done in Fall 1980 and Spring 1981 at 25 sites (Fig. 1) from the mouth of Smoke Creek north to the mouth of Tonawanda Creek on the Niagara River. Verification sampling was done in 1981 and 1982 at areas indicated to have high PAH concentration by the preliminary survey. This sampling was done to confirm the preliminary sampling results and narrow the area of suspected PAH input. Analyzed media included water, polypropylene substrates, and sediment.

Grab or composite water samples were taken for PAH analyses. Two liter grab samples were taken on two subsequent days from Smoke Creek. Allied Chemical, Buffalo Color, Bethlehem Steel, and the Lackawanna Sewer Treatment Plant outfalls were sampled with an ISCO toxics sampler. Water samples were composited in a 10 L bottle at a rate of 100 ml/15 min. over a 24 h period. The Buffalo Sewer Authority outfall was also sampled with an ISCO toxics sampler at the rate of 200 ml/15 min. over a 24 hr. period. Samples were composited into a 20 L container. Sediment samples were taken by Ponar Dredge.

STATISTICAL TREATMENT

Relative proportions of PAH were used to characterize sediment sampling sites. The degree of similarity among sites was calculated with n-space Euclidean geometry where n is the number of different PAH compounds analyzed. Small n-space distances indicate similarity among sites based on the relative proportions of PAH. The computer software used to generate the distances produces a cluster map that shows the clusters of sites and, therefore, which sites are more closely associated based on the relative PAH composition.

Cluster analyses of PAH distribution in sediments were done using the SAS (SAS 1979) cluster analysis program. Eighteen PAH compounds were quantified in sediment analyses, but only PAH with low solubility that would be expected to be retained in sediment were used in the cluster analyses. These were benzo(e)pyrene, chrysene, perylene, benzo(a)pyrene and dibenzo(a,h)anthracene. Cluster analyses were performed on the relative percentage of these five PAH's and they identified differences in PAH composition among sites studied. The cluster analysis is based on the following equation: $x = (a_1 - b_1)^2 + (a_2 - b_2)^2 \ldots\ldots (a_n - b_n)^2$, where a_n is the percent of total PAH composition of a specific PAH at one site and b_n is the percent of total PAH composition of the same compound at another site. Small values of x should therefore indicate a similarity in PAH composition between sites, while relatively large values of x indicate a dissimilarity in PAH composition between sites. The SAS program carries out a multistep process. It begins by forming one cluster for each observation in the analysis. The two closest clusters are then combined into one cluster, then the two new closest clusters are combined into a single cluster, and so on until all observations are in a single cluster. This process is depicted on a cluster map (see Fig. 11) by lines of asterisks joining each cluster as it is formed starting from the top of the page and reading down. Sites which have a similar PAH composition should cluster together at an early stage in this analysis.

RESULTS AND DISCUSSION

PRELIMINARY SURVEY

The twenty-five sites sampled by artificial substrate in Spring 1981, including 13 sites which were sampled in Fall 1980, are shown in Fig. 1. Chromatograms of extracts were ranked qualitatively for total PAH concentration (Table 1; Appendix A). Five broad groupings were established: neglible, low, medium, medium high, and high. Each grouping has an approximate tenfold difference in total PAH accumulation from its adjacent group. Unless otherwise indicated, no attempt was made to quantify PAH accumulation in artificial substrates throughout this investigation. The distribution of sites so grouped is indicated in Figure 1. The site ranking of the 13 identical sites sampled in 1980 versus 1981 is similar with the exception of Two Mile Creek. On the basis of the preliminary sampling data, five areas which had medium to high PAH accumulation during at least one sampling period were considered for further investigation. These were: 1) Two Mile Creek, 2) Buffalo Sewer Authority, 3) Buffalo River, 4) Lackawanna-Union Canals, and 5) Smoke Creek.

The five sampling sites identified by the preliminary survey as having significant PAH inputs were in areas that had potential anthropogenic sources of these compounds such as iron and steel manufacturing operations (Smoke Creek, Union and Lackawanna Ship Canals, and Buffalo River), oil storage facilities (Two Mile Creek), municipal wastewater treatment facilities (Buffalo Sewer Authority) or other industrial activities (Buffalo River). Four areas identified as having PAH inputs in the preliminary survey - Buffalo River, Smoke Creek, Union and Lackawanna Ship Canals, and Two Mile Creek were subsequently sampled

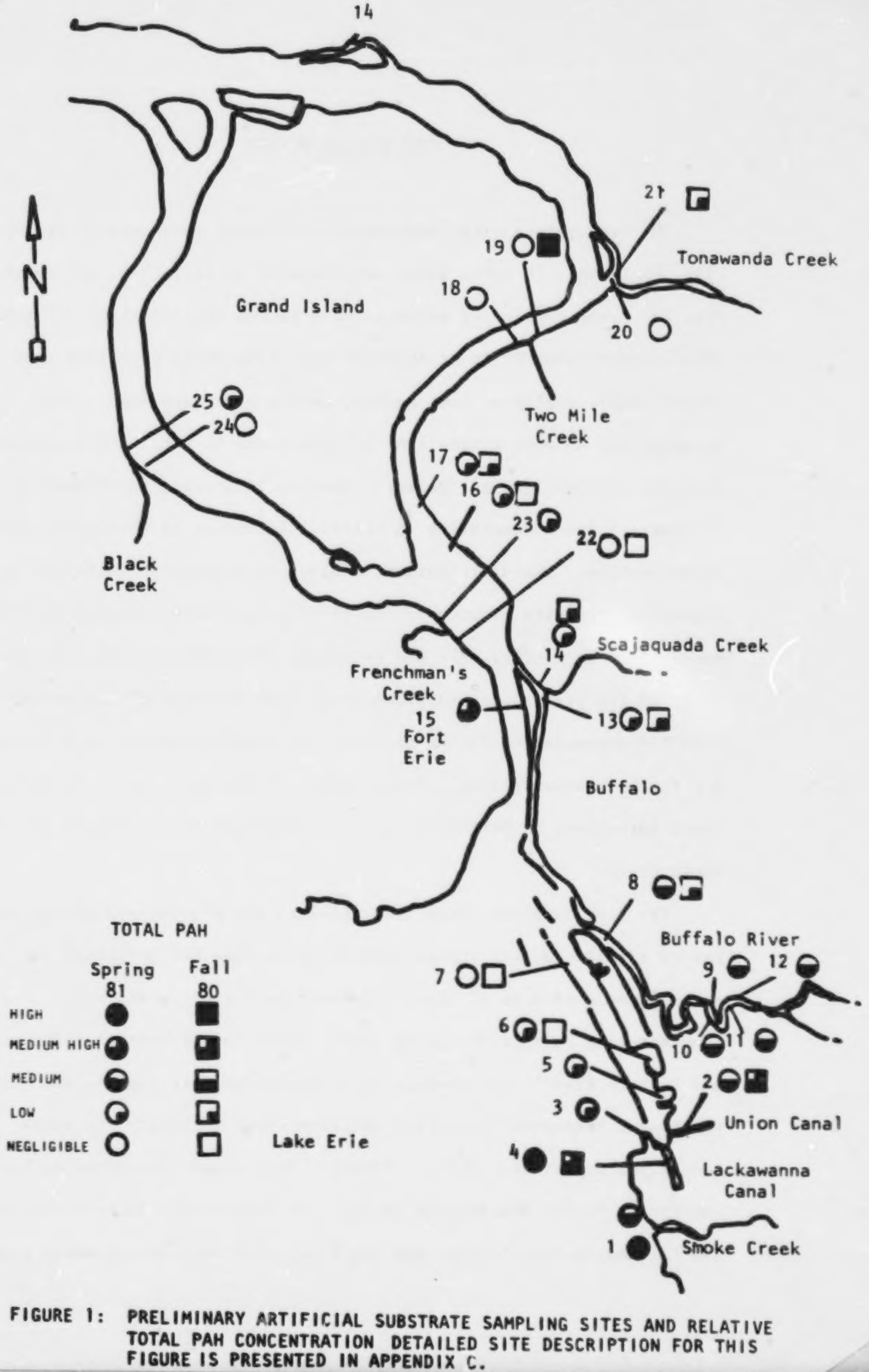

14
21
19
Tonawanda Creek
18
Grand Island
20
N
25
24
Two Mile Creek
17
16
23
22
Black Creek
Scajaquada Creek
14
Frenchman's Creek
15
Fort Erie
13
Buffalo
8
TOTAL PAH
Buffalo River
Spring 81
Fall 80
7
9
12
HIGH
MEDIUM HIGH
MEDIUM
LOW
NEGLIGIBLE
6
10
11
5
2
3
Union Canal
Lake Erie
4
Lackawanna Canal
1
Smoke Creek

FIGURE 1: PRELIMINARY ARTIFICIAL SUBSTRATE SAMPLING SITES AND RELATIVE TOTAL PAH CONCENTRATION DETAILED SITE DESCRIPTION FOR THIS FIGURE IS PRESENTED IN APPENDIX C.

TABLE 1. PAH SCREENING RESULTS (RANK-GROUP)

SAMPLE SITE		Fall "80"	5/81 wk. 2	5/81 wk. 4	6/81 wk. 1	6/81 wk. 2	6/81 wk. 3
1.	Smokes Creek			6-M			2-MH
2.	Union Canal	3-MH	1-M			3-MH	
3.	Lackawanna Canal (Mouth)				19-L		
4.	Lackawanna Canal	2-MH	8-H			9-M	
5.	Small Boat Harbor A		27-N				
6.	Small Boat Harbor B	4-L	26-N				
7.	Buffalo River A (Breakwall)	10-N	20-N				25-N
8.	Buffalo River B (Naval Park)	5-L	12-M				5-M
9.	Allied Chemical (L bank below)						7-M
10.	Allied Chemical (R bank below)						10-M
11.	Republic Steel						11-M
12.	Buffalo Color						15-L
13.	Scajaquada A	6-L					16-L
14.	Scajaquada B	9-N					
15.	Buffalo Sewer Authority				4-MH		
16.	Sheridan Drive (foot of)	11-N		13-L			
17.	Niagara Mohawk	7-L	18-L				
18.	Two Mile Creek A	1-H		23-N			
19.	Two Mile Creek B			24-N			
20.	Tonawanda Creek A			22-N			
21.	Tonawanda Creek B	8-L					
22.	Frenchman's Creek A		21-N				
23.	Frenchman's Creek B	12-N		17-L			
24.	Black Creek A	13-N					
25.	Black Creek B			19-L			

Group

H - High
MH - Medium High
M - Medium
L - Low
N - Negligible

with artificial substrates, or water and sediment samples were taken for PAH analyses to assist in source identification. This verification sampling was planned in conjunction with Region 9 NYSDEC staff, Central Office NYSDEC staff, and the contractor. The Buffalo Sewer Authority was monitored directly in the discharge and, therefore, no further source identification was required. However, water samples were taken to assess PAH concentrations in the discharge. These sites will be discussed in detail under verification sampling.

The criteria for selecting a site from the preliminary survey for further investigation was based on a ranking of medium to high during a minimum of one sampling period by artificial substrate. Artificial substrates were consistent in the accumulation of total PAH in the preliminary survey with the exception of those at the Buffalo River at Naval Park and Two Mile Creek. The Buffalo River at Naval Park (Fig. 1) artificial substrate samples gave a reading of low and medium during two different sampling periods. At this location in the Buffalo River, there is a characteristic flow reversal which may account for low PAH level in the artificial substrate on one occasion and a medium reading on another occasion, because the PAH contamination from upstream may not be consistently carried downstream as would be expected in most riverine systems. The Two Mile Creek substrate results of a high and a negligible level in artificial substrates may result from the extremly intermittent nature of the sources of PAH in this drainage. These results will be discussed in detail under the verification sampling.

The results from the preliminary survey indicate that artificial substrates were effective in screening large areas for PAH inputs. These substrates have several advantages for ambient monitoring over conventional environmental samples. These are 1) ability to place them almost anywhere in an aquatic environment, 2) integration of contaminant exposure over time, and 3) identification of the presence of PAH in the water column. The use of an artifical substrate offers an alternative to monitoring of water, sediment, or biota that can overcome some of the problems involved with contaminant monitoring of these strata. Water sample monitoring may miss occasional, but significant discharges of PAH. Sediment sampling may reflect old discharges which may not have any significance to environmental or human health, because the contaminants are bound to the sediments. Conversely, leaching of PAH from sediments into the surface waters can be detected by use of the artificial substrates. Sampling biota may provide integration of contaminant exposure over time, however contaminant monitoring is complicated by the mobility of the organisms being monitored. The artificial substrates overcome these problems in water, biological, and sediment monitoring.

VERIFICATION SAMPLING

Following the preliminary survey, site specific sampling was carried out for those areas having medium to high total PAH concentrations as indicated by the preliminary survey. These areas were the Buffalo Sewer Authority, Buffalo River, Smoke Creek, the Union and Lackawanna Ship Canals, and Two Mile Creek. This sampling included additional sampling with artificial substrates, water, or sediment collections. Artificial substrates were used to focus more clearly on the area of suspected discharge. Sampling of sediment and water was used to suggest or confirm sources of PAH. PAH sediment sampling locations are shown in Figs. 2-5.

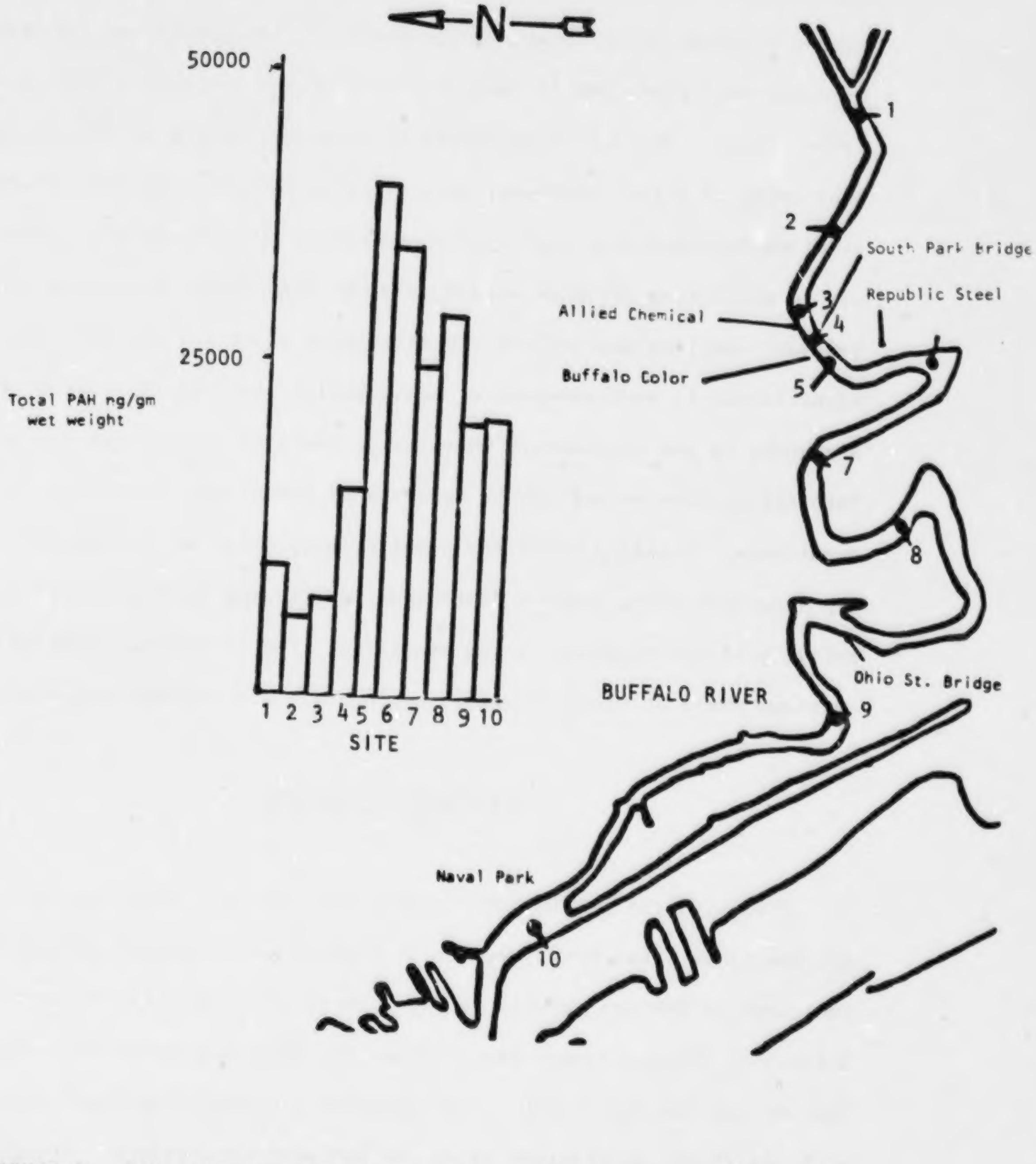

N
50000
25000
Total PAH ng/gm wet weight
1 2 3 4 5 6 7 8 9 10
SITE
1
2
South Park Bridge
3
Republic Steel
Allied Chemical
4
Buffalo Color
5
7
8
Ohio St. Bridge
BUFFALO RIVER
9
Naval Park
10

FIGURE 2: PAH SEDIMENT SAMPLING SITES. BUFFALO RIVER WITH RELATIVE TOTAL PAH CONCENTRATION. DETAILED SITE DESCRIPTION FOR THIS FIGURE IS PRESENTED IN APPENDIX C.

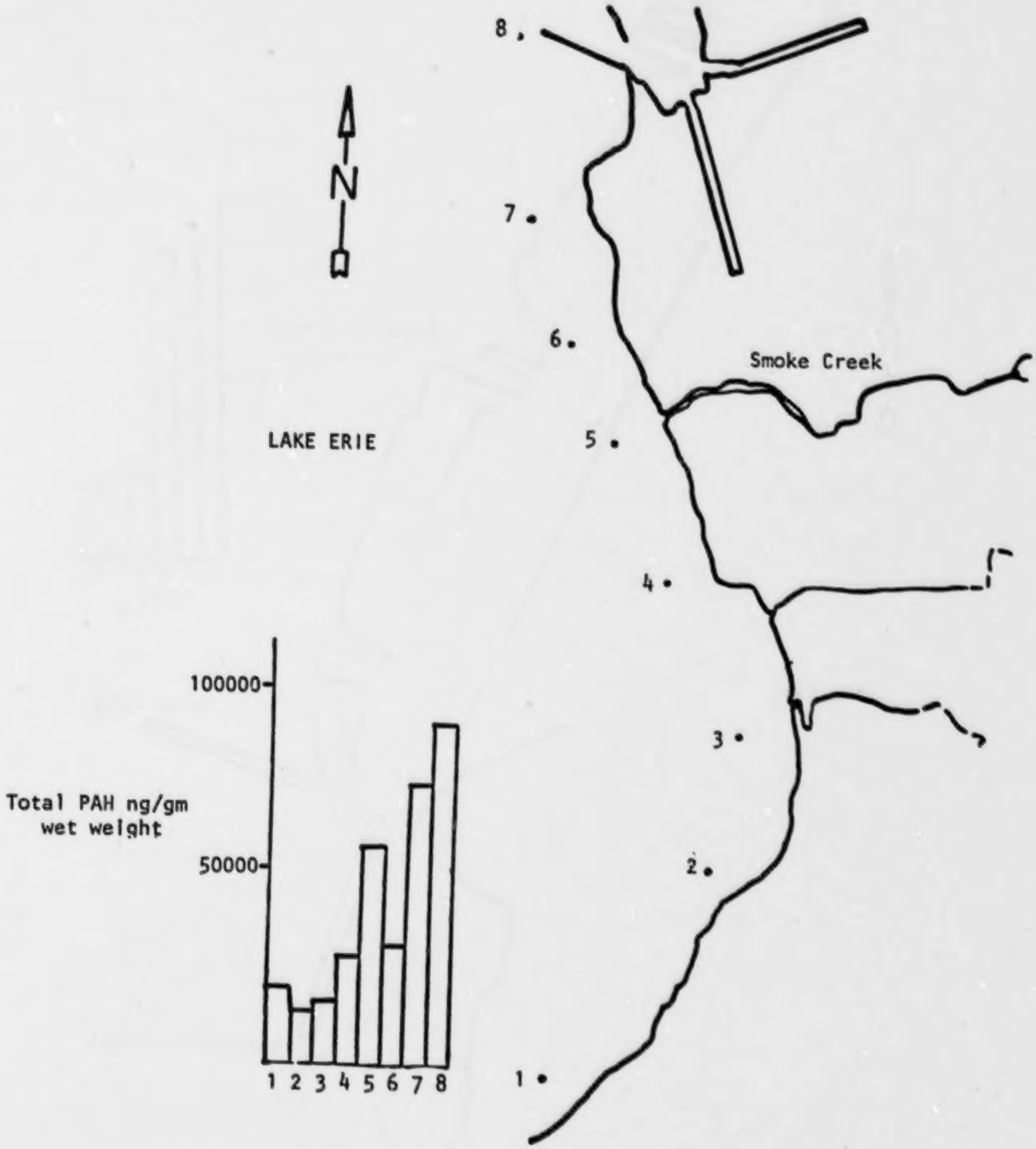

8
7
6
5
4
3
2
1
N
Smoke Creek
LAKE ERIE
100000
50000
Total PAH ng/gm wet weight
1 2 3 4 5 6 7 8

FIGURE 3: PAH SEDIMENT SAMPLING STIES. SMOKE CREEK TRANSECT IN LAKE ERIE WITH RELATIVE TOTAL PAH CONCENTRATION DETAILED SITE DESCRIPTION FOR THIS FIGURE IS PRESENTED IN APPENDIX C.

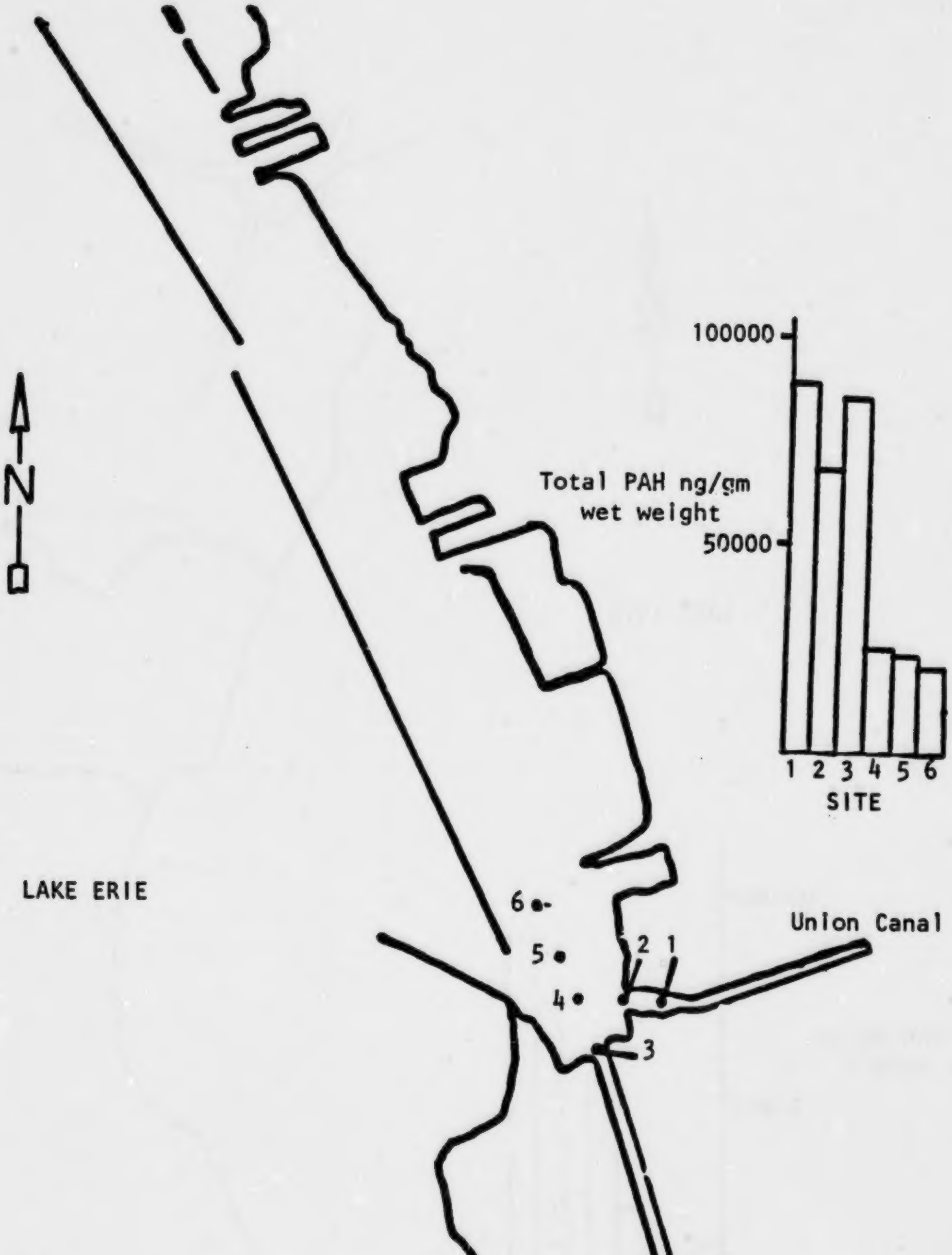
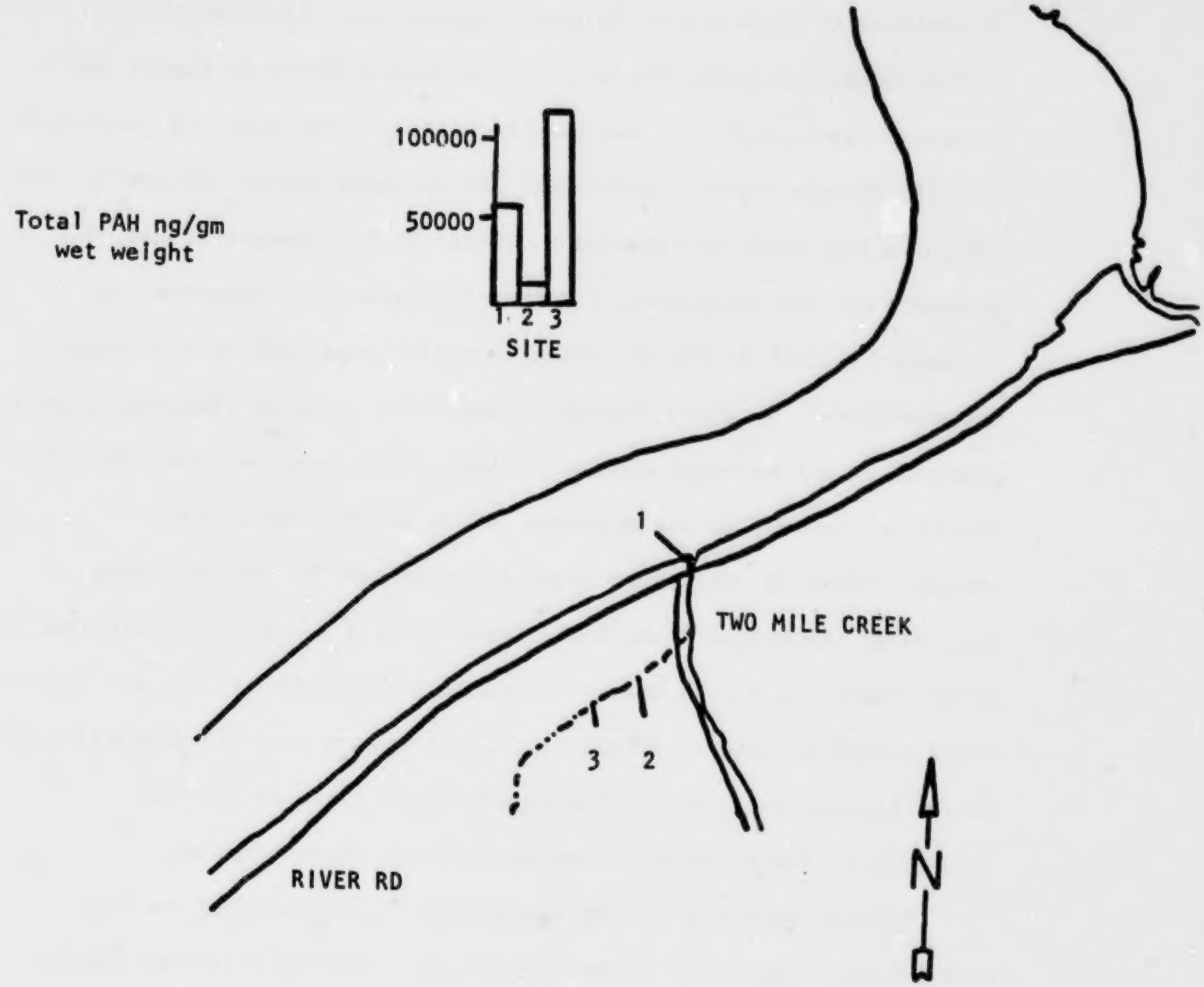

N
100000
50000
Total PAH ng/gm wet weight
1 2 3 4 5 6
SITE
LAKE ERIE
6
5
4
2
1
3
Union Canal
Lackawanna Canal

FIGURE 4: PAH SEDIMENT SAMPLING SITES AT UNION AND LACKAWANNA CANALS WITH RELATIVE PAH CONCENTRATION. DETAILED SITE DESCRIPTION FOR THIS FIGURE IS PRESENTED IN APPENDIX C.



Total PAH ng/gm wet weight
100000
50000
1
2
3
SITE
1
TWO MILE CREEK
3
2
RIVER RD
N

FIGURE 5: PAH SEDIMENT SAMPLING SITES AT TWO MILE CREEK WITH RELATIVE PAH CONCENTRATION. DETAILED SITE DESCRIPTION FOR THIS FIGURE IS PRESENTED IN APPENDIX C.

In addition to these sites, sediment samples were taken at the junctions of Frenchmans and Black Creeks with the Niagara River in Canada and in Tonawanda Creek (U.S.A.), one quarter mile upstream from its confluence with the Niagara River. Individual PAH sediment concentrations for all locations are shown in Appendix B (Tables 1-7). Concentrations of phenanthrene, benzanthracene and benzo(a)pyrene are summarized in Appendix D (Table 8) for all sites to allow comparison of a 3-ringed (phenanthrene), 4-ringed (benzanthracene) and 5-ringed (benzo(a)pyrene) compound at all sediment sampling sites. Water samples were taken from discharges to confirm the presence of PAH in effluents. PAH concentrations in unfiltered water are reported for the following locations: Bethlehem Steel/Smoke Creek (Table 2), Buffalo Color/Buffalo River (Table 3), Allied Chemical/Buffalo River (Table 4) and the Buffalo Sewer Authority outfall (Table 5). Verification sampling with artificial substrates and associated sediment and water analyses for PAH consistently demonstrated contamination with these compounds.

Sediment sampling for PAH contamination corroborated the PAH contamination indicated by the substrates. This relationship between relative grouping of sites and sediment contamination of PAH for 10 sites having preliminary artificial substrate sampling and verification sediment sampling locations in common is shown in Fig. 6. Sites ranking medium to high by artificial substrate determinations tended to have higher concentrations of PAH in sediment. Conversely, sites ranking low or negligible by artificial substrates tended to have lower concentrations in sediment. Tonawanda Creek is an exception to this overall pattern. PAH concentrations in sediment at Tonawanda Creek, which artificial substrate sampling indicated had low concentrations of

TABLE 2. PAH CONCENTRATION IN WATER (ng/L) SAMPLES FROM SMOKE CREEK, BETHLEHEM STEEL OUTFALLS TO SMOKE CREEK AND THE LACKAWANNA SEWAGE TREATMENT PLANT OUTFALL TO SMOKE CREEK.

COMPOUND	Bethlehem Steel Outfall 217	Bethlehem Steel Outfall 225	Lackawanna STP Outfall	Smoke Creek Downstream of South Return Trench	Return Trench South of Mouth of Smokes Creek	Smoke Creek Immediately Upstream of Bethlehem Steel
FLUORENE	ND*	ND	ND	ND	ND	ND
PHENANTHRENE	ND	ND	ND	ND	ND	ND
ANTHRACENE	ND	ND	ND	ND	ND	ND
FLUORANTHENE	1400	56000	3500	240	180	30
MePHENANTHRENE	ND	ND	ND	ND	ND	ND
PYRENE	420	16000	260	91	95	66
MeANTHRACENE	ND	ND	ND	ND	ND	ND
BENZOFLUORENE	ND	ND	ND	ND	ND	ND
BENZANTHRACENE	27	3000	18	0.3	1.8	3.3
CHRYSENE	70	7500	41	3.8	9.2	5.8
BENZO(e)PYRENE	ND	ND	ND	ND	ND	ND
PERYLENE	ND	ND	ND	ND	ND	ND
BENZO(b)FLUORANTHENE	30	1900	7.6	4.4	5.5	3.4
BENZO(k)FLUORANTHENE	1.2	970	50	1.3	1.5	1.4
BENZO(a)PYRENE	2.5	970	11	2.7	3.0	3.2
DIBENZ(a,h)ANTHRACENE	0.7	97	2.4	0.7	0.6	0.7
BENZO(g,h,i)PERYLENE	3.3	1500	9.3	3.7	2.4	2.5
INDENO(1,2,3-c,d)PYRENE	ND	ND	ND	ND	ND	ND
TOTAL	2000	88000	3900	350	300	120

*ND - Not Detected

TABLE 3. PAH CONCENTRATIONS IN WATER FROM BUFFALO COLOR WATER OUTFALLS AND INTAKE

COMPOUND	Concentration (ng/L)		
	Intake	Outfall 006	Outfall 011
FLUORENE	ND*	ND	ND
PHENANTHRENE	ND	ND	ND
ANTHRACENE	ND	ND	ND
FLUORANTHENE	1.3	5.4	6.0
MePHENANTHRENE	ND	ND	ND
PYRENE	4.2	5.2	ND
MeANTHRACENE	ND	ND	43
BENZOFLUORENE	ND	ND	ND
BENZANTHRACENE	0.2	ND	ND
CHRYSENE	0.4	0.3	0.6
BENZO(e)PYRENE	ND	0.4	1.1
PERYLENE	ND	ND	ND
BENZO(b)FLUORANTHENE	0.3	ND	ND
BENZO(k)FLUORANTHENE	0.2	0.3	0.6
BENZO(a)PYRENE	0.8	0.2	0.3
DIBENZO(g,h,i)PERYLENE	0.2	0.7	0.9
BENZO(g,h,i)PERYLENE	0.3	0.1	0.1
INDENO(1,2,3-c,d)PYRENE	ND	13	0.4
		ND	ND
TOTAL	7.9	25	53

*ND - Not Detected

TABLE 4. PAH CONCENTRATIONS IN WATER FROM ALLIED CHEMICAL OUTFALLS TO BUFFALO RIVER

COMPOUND	Concentration (ng/L)		
	Outfall 001	Outfall 003	Outfall 004
FLUORENE	ND*	ND	ND
PHENANTHRENE	ND	ND	ND
ANTHRACENE	ND	ND	ND
FLUORANTHENE	ND	ND	ND
MePHENANTHRENE	ND	1.2	5.4
PYRENE	ND	ND	ND
MeANTHRACENE	2.1	1.1	2.0
BENZOFLUORENE	ND	ND	ND
BENZANTHRACENE	ND	ND	ND
CHRYSENE	0.2	0.1	0.1
BENZO(e)PYRENE	0.3	ND	0.6
PERYLENE	ND	ND	ND
BENZO(b)FLUORANTHENE	ND	ND	ND
BENZO(k)FLUORANTHENE	0.2	0.6	0.1
BENZO(a)PYRENE	0.1	ND	0.1
DIBENZ(a,h)ANTHRACENE	0.5	0.5	0.7
BENZO(g,h,i)PERYLENE	0.1	ND	0.7
INDENO(1,2,3-c,d)PYRENE	0.2	0.1	7.5
	ND	ND	ND
TOTAL	3.7	3.6	17

*ND - Not Detected

TABLE 5. PAH CONCENTRATIONS IN BUFFALO SEWER AUTHORITY OUTFALL WATER (ng/L)

COMPOUND	CONCENTRATION
FLUORENE	ND*
PHENANTHRENE	ND
ANTHRACENE	ND
FLUORANTHENE	5.7
MePHENANTHRENE	ND
PYRENE	9.2
MeANTHRACENE	ND
BENZOFLUORENE	ND
BENZATHRACENE	0.5
CHRYSENE	5.5
BENZO(e)PYRENE	ND
PERYLENE	ND
BENZO(b)FLUORANTHENE	0.7
BENZO(k)FLUORANTHENE	0.3
BENZO(a)PYRENE	0.8
DIBENZ(a,h)ANTHRACENE	0.1
BENZO(g,h,i)PERYLENE	0.5
INDENO(1,2,3-c,d)PYRENE	ND
Total PAH Concentration	23

*ND - Not Detected

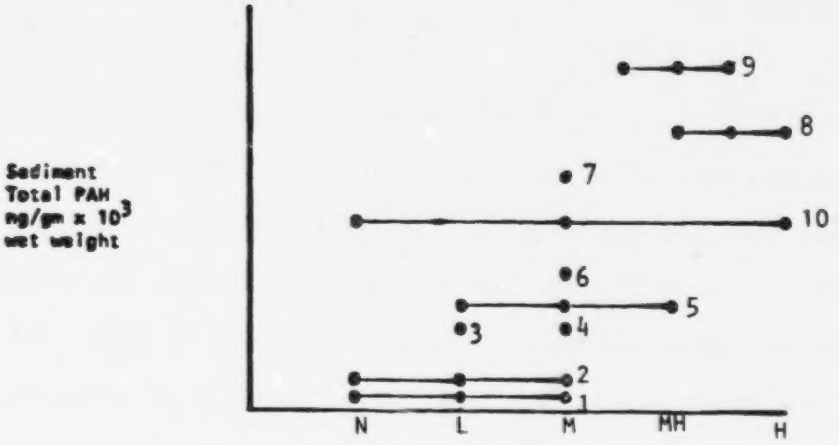


Figure 6: Total PAH Sediment Concentrations (wet weight) and Corresponding Artificial Substrate Total PAH Group for Similar Stations. (Only ten stations appear because sediments were not available or taken from the other substrate sampling stations. If two substrate samples were taken at the same site the mean of the groups is indicated by a filled in circle.). DETAILED SITE DESCRIPTION FOR THIS FIGURE IS PRESENTED IN APPENDIX C.

Key

1. - Mouth of Black Creek
2. - Mouth of Frenchman's Creek
3. - Mouth of Tonawanda Creek
4. - Buffalo River at South Park Bridge
5. - Buffalo River at Naval Park
6. - Buffalo River at Republic Steel
7. - Buffalo River at Buffalo Color
8. - Lackawanna Canal
9. - Union Canal
10.- Two Mile Creek

PAH, had sediment concentrations similar to those sites ranked medium by artificial substrate sampling. This may indicate that PAH in sediments of Tonawanda Creek are not entering the water column, and therefore are not available to be accumulated in artificial substrates.

The results from the verification sampling of the five areas identified as having suspected PAH discharges are discussed below.

Buffalo Sewer Authority

No further source identification was required at this site because artificial substrates were placed directly in the discharge. A water sample from this discharge was taken for analysis. The total PAH concentration of 23 ng/L (Table 5) was a relatively low value compared to those for PAH in wastewater treatment effluents as summarized by Neff (1979). This would amount to a loading of 17 gm of total PAH to the river per day. Although this is a relatively small amount of PAH, there may be considerable variation in the PAH burden of the wastewater from day to day. Consequently, the Buffalo Sewer Authority may require additional water sampling to determine the PAH load to the Niagara River.

Buffalo River

Eleven sites were sampled by artificial substrates in the Buffalo River (Fig. 7). All sites sampled had evidence of PAH contamination (Table 6). Sites 4 and 7 gave high values that suggested point source contributions. Sites 4 and 7 are near effluents from Allied Chemical, Buffalo Color, and Republic Steel. They were subsequently targeted for a further study which is described below.

Artificial substrates were placed near the two Allied Chemical effluents, Buffalo Color, and the two Republic Steel effluents. There appeared to be a strong PAH source near the South Park bridge (Fig. 8).

TABLE 6. PAH CONCENTRATIONS
ARTIFICIAL SUBSTRATES FROM BUFFALO RIVER

	Phenanth.	Anthracene	Fluoranth.	MePhenanth.	MeAnth.	Benzofluor.	Benzanth.	Chrysene	Benz(e)pyr.	Perylene	Benz(a)pyr.	Dibenz(a,h).	Coronene	Total PAH
Site 1	15[1]	1.9	54	9.9	8.4	8.1	12	25	12.8	23	6.7	3.3	-	180[3]
Site 2	17	2.8	95	16	12	22	17	21	10.8	10	5.5	2.3	-	232
Site 3	14	1.9	74	13	12	28	36.6	45	16.1	22	6.4	5.4	-	270
Site 4	6.8[2]	1.8	220	27	24	150	200	180	82.9	59	4.6	6.2	LP	960x5
Site 5	10	0.9	3.7	7.4	20	26	38	12	11.5	4.8	-	-	-	135
Site 6	12	1.8	77	13	13.5	27	32	44	13.3	14	2.8	-	-	250
Site 7	13	3.1	140	22	37	78	130	140	74.5	84	38	17	LP	777
Site 8	14	3.4	110	16	19	37	36	48	22.4	17	8.1	2.4	-	333
Site 9	12	2.0	72	13	13	28	36	41	15.5	22	4.0	0.4	-	259
Site 10	12	1.5	29	4.3	3.3	2.5	1.1	9.5	9.5	8.7	9.6	-	-	91
Site 11	15	2.2	40	7.8	7.7	9.8	-	14	20.3	16	11	2.4	-	146

[1] All concentrations are in nanograms per substrate

[2] 1 ul injected - multiply by 5 for equivalent values ie. 4781.0

[3] based on identified peaks only

LP significant peak in this area

A second artificial substrate sampling was done one month later to supplement results of previous investigations. Artificial substrates were tiered in relation to a probable downstream flow from the South Park Bridge area, and an upstream flow from Republic Steel to distinguish between a possible erroneous analysis resulting from upstream movement of PAH from downstream sources due to flow reversal. Results of these analyses are shown in Fig. 8. The distribution of PAH contamination at this site indicates that it is unlikely that the high levels associated with the South Park bridge are due to upstream movement of PAH from other effluents. However, the possibility of pooling of PAH at this site should also be considered as a possible reason for the consistently high result.

PAH sediment samples were taken throughout the Buffalo River (Fig. 2) in addition to artificial substrate samples (Fig. 7). Sediment samples had their highest PAH concentrations immediately downstream from the South Park bridge (Fig. 2) which corroborates the source of PAH indicated by the high accumulation of PAH by artificial substrates at this location (Table 6).

Water samples from outfalls of two dischargers in this area had PAH in their water samples (Table 3). Buffalo Color outfall 011 was approximately 1000 yds. upstream from the south Park Bridge. This discharge had PAH concentrations seven times higher than intake water. This outfall may be one point source of the high PAH concentrations found in the area of the South Park Bridge. Although most PAH compounds were not found in Buffalo Color outfalls (Table 3), pyrene exhibited the highest concentration of any PAH from the outfalls sampled in this area (Tables 3 & 4). The highest concentration of pyrene found in Buffalo

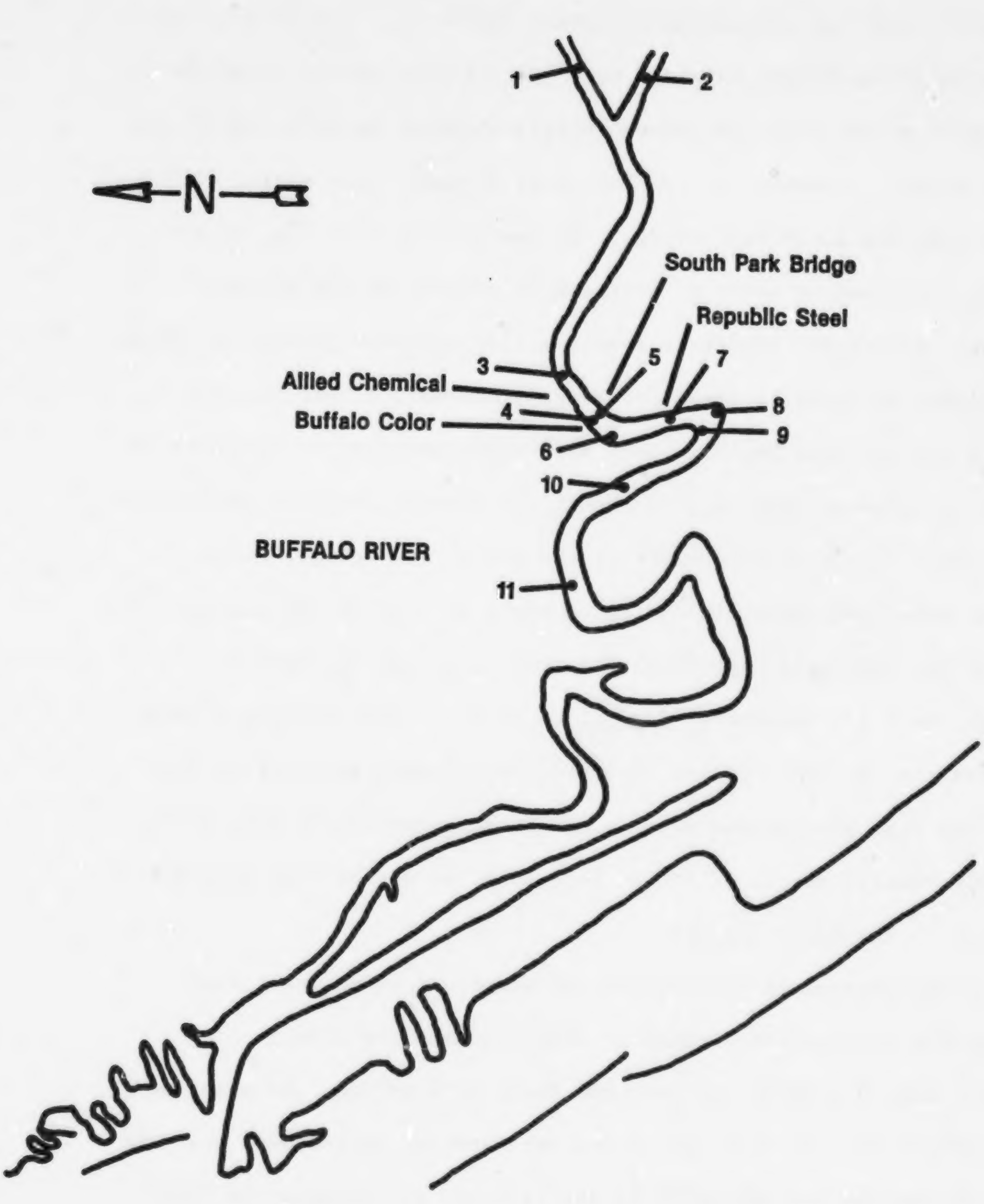

1
2
N
South Park Bridge
Republic Steel
3
5
7
Allied Chemical
4
8
Buffalo Color
9
6
10
BUFFALO RIVER
11

FIGURE 7: ARTIFICIAL SUBSTRATE SAMPLING SITES IN BUFFALO RIVER. DETAILED SITE DESCRIPTION FOR THIS FIGURE IS PRESENTED IN APPENDIX C.

River sediment was also at this location. Allied Chemical outfalls did not exhibit high concentrations of pyrene (Table 4). Allied Chemical or Buffalo Color discharges have not been conclusively proven to be the dischargers of the high PAH concentrations observed in this area of the Buffalo River. However, it is clear that a significant source of PAH is present near the South Park bridge. As can be seen from Fig. 2, total PAH concentrations in sediment decrease in subsequent downstream stations. Artificial substrate sampling also suggested inputs of PAH in the vicinity of Republic Steel discharges, however, direct effluent sampling was not done because these discharges were not in operation at the time of planned sampling. Although the present evidence indicates a point source in the Buffalo River at the South Park bridge, further effluent water and sediment monitoring would be required to pinpoint the cause of the extremely high total PAH concentrations in sediment. Although there are industrial facilities in this area, release of high concentrations of PAH from the type of chemical manufacturing or dye operations that are present here is not to be expected (US EPA, 1979). Another potential source of PAH at this location may be from groundwater leachates to the Buffalo River.

The percentages of constituent PAH compounds in sediment vary considerably between those taken at sediment sampling site 5 (Table 7, Fig. 9), which was near the South Park bridge, and sampling site 6 (Table 7). Benzo(e)pyrene was not detected in sediment near the South Park bridge but was found in the vicinity of the Republic Steel outfalls (Site 6, Table 7) to this area at concentrations of 130 ng/gm organic weight. An outfall of Donner-Hanna Coke also discharges at this location. Benzo(a)pyrene concentrations approximately double at site 6

TABLE 7. PAH SEDIMENT CONCENTRATIONS (ORGANIC WEIGHT ng/mg) AT BUFFALO RIVER SITES 5 and 6

COMPOUND	CONCENTRATION	
	Site 5	Site 6
FLUORENE	13	20
PHENANTHRENE	200	110
ANTHRACENE	70	42
FLUORANTHENE	210	100
MePHENANTHRENE	29	28
PYRENE	450	220
MeANTHRACENE	20	17
BENZOFLUORENE	190	180
BENZANTHRACENE	42	80
CHRYSENE	7	54
BENZO(e)PYRENE	ND*	130
PERYLENE	280	240
BENZO(b)FLUORANTHENE	ND	62
BENZO(k)FLUORANTHENE	18	36
BENZO(a)PYRENE	39	79
DIBENZ(a,h)ANTHRACENE	130	14
BENZO(g,h,i)PERYLENE	14	73
INDENO(1,2,2-c,d)PYRENE	16	51
TOTAL	1700	1500

*ND - Not Detected

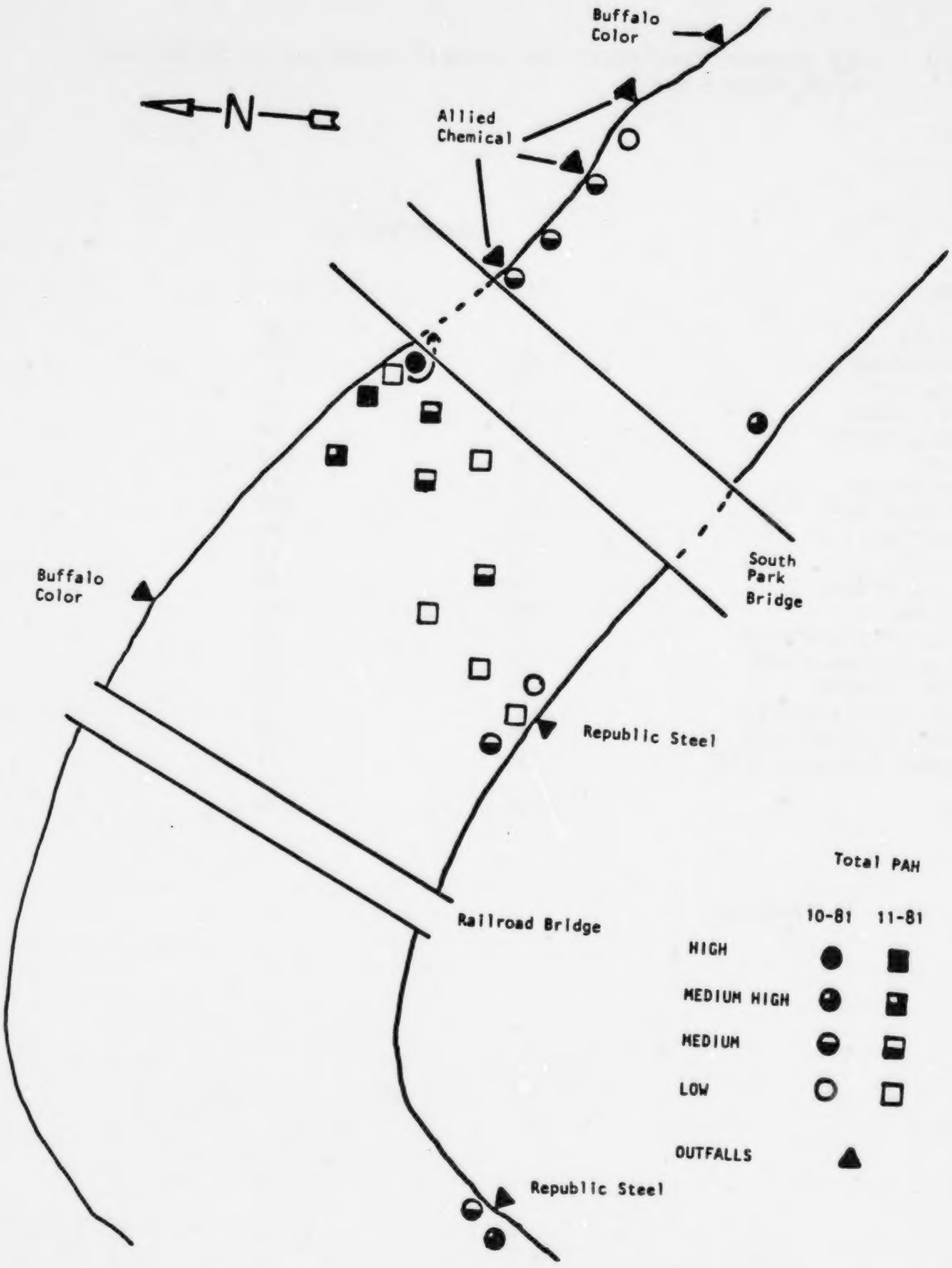

Buffalo Color
N
Allied Chemical
South Park Bridge
Buffalo Color
Republic Steel
Railroad Bridge
Republic Steel
Total PAH
10-81
11-81
HIGH
MEDIUM HIGH
MEDIUM
LOW
OUTFALLS

FIGURE 8: BUFFALO RIVER ARTIFICIAL SUBSTRATE SAMPLING SITES NEAR SOUTH PARK BRIDGE AND TOTAL PAH

as compared to 5 (Table 7; Fig. 9) even though total PAH concentrations decrease. However, artificial substrates do not reflect this increase in benzo(a)pyrene and benzo(e)pyrene concentrations (Table 6). High concentrations of benzo(a)pyrene have been associated with foundry (Schimberg et al., 1980) and coking operations (Lao et al., 1975). Benzo(e)pyrene has also been reported in air samples from foundries. Therefore, the increase of these two compounds in the sediments could be expected. The operations at the Republic Steel and Donner-Hanna Coke facilities have been curtailed and consequently the presence of PAH presumably attributable to these facilities may represent old inputs. The absence of increases of benzo(a)pyrene and benzo(e)pyrene concentrations in substrates placed at the South Park bridge and at Site 6 may be due to the absence of ongoing discharges from Donner-Hanna and Republic Steel. Chrysene concentrations also significantly increase in concentration from 7 ng/gm organic weight to 54 ng/gm (Table 7) from sediment sampling sites 5 to 6. Chrysene has been reported at extremely high concentrations in raw wastewater of foundries and iron and steel manufacturers. Maximum concentrations for foundries and iron and steel manufacturing were reported as 1,300 ug/L and 2,200 ug/L respectively with mean values of 1,100 ug/L and 94 ug/L (USEPA 1979).

The presence of elevated PAH concentrations in drainage basins of highly urbanized areas such as the Buffalo River is not unusual (Herman 1981, Wong 1981). The PAH concentration in the sediments, however, are extremely high. Eadie et al. (1982) reported sediment concentrations of total PAH of up to 770 ug/kg in western Lake Erie associated with a power plant while the total PAH concentrations in Buffalo River sediments were as high as 44,000 ug/kg wet weight.

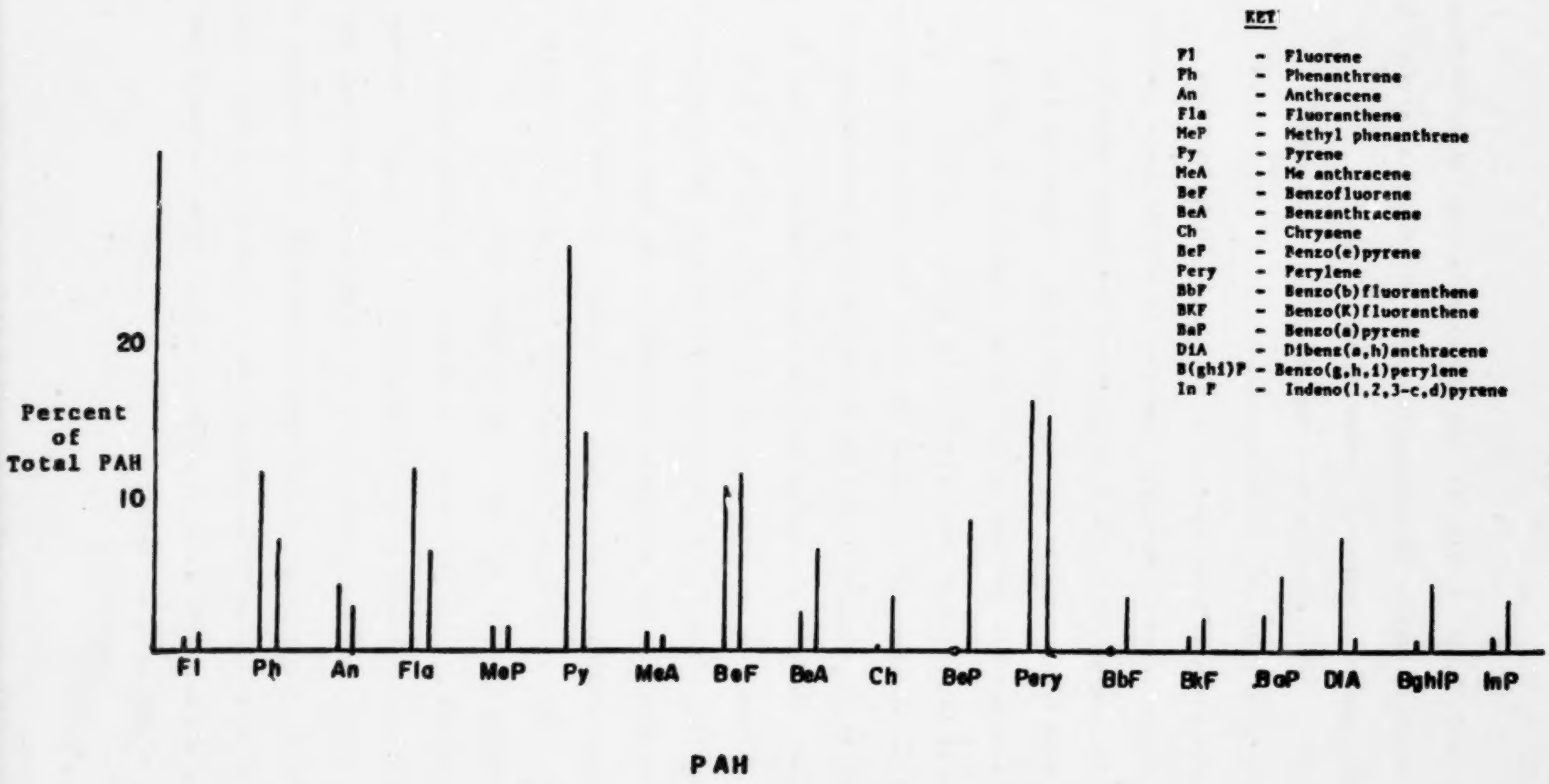


Figure 9: Present Composition of Total PAH Compounds in Sediment (Organic Weight) at Buffalo River Sites 5 and 6. First Line of Pair is Site 5.

Smoke Creek and Union and Lackawanna Canals

Smoke Creek and the Union and Lackawanna Canal areas are treated together because the suspected source of the PAH pollution of this area is the same for both.

PAH concentrations in the artificial substrates placed in the south branch of Smoke Creek were considerably higher than in those in the north branch (Fig. 10, Table 8). A heavy rain had fallen and the source of PAH may have been a sewer overflow discharging to the south branch of Smoke Creek. However, another DEC sampling program for contaminants (Spring 1982) in sewer overflows did not find high PAH concentrations in this sewer overflow. PAH concentrations at the mouth of Smoke Creek were higher than those at any other station except the south branch station, and this suggests an input of PAH from the Bethlehem Steel property.

A strong contribution of PAH was apparent in the area of the Lackawanna and Union Ship Canals (Fig. 10), however an artificial substrate placed directly in the Union Canal had a relatively low PAH concentration (Table 8).

PAH analyses of water samples from Bethlehem Steel outfalls and in the portion of Smokes Creek running through Bethlehem Steel property revealed the highest PAH concentrations in water found in this study (Table 2). Fluoranthene occurred in the highest concentration in all water samples while pyrene occurred in the second highest concentration. Compounds such as fluoranthene, chrysene, and benzo(a)pyrene, all present in Bethlehem Steel outfall samples, have been reported from other foundry and ferrous metal manufacturing operations (USEPA, 1979). The concentration of total PAH (organic weight) at Lake Erie site 8 exhibits an approximate four fold increase in concentration over total PAH

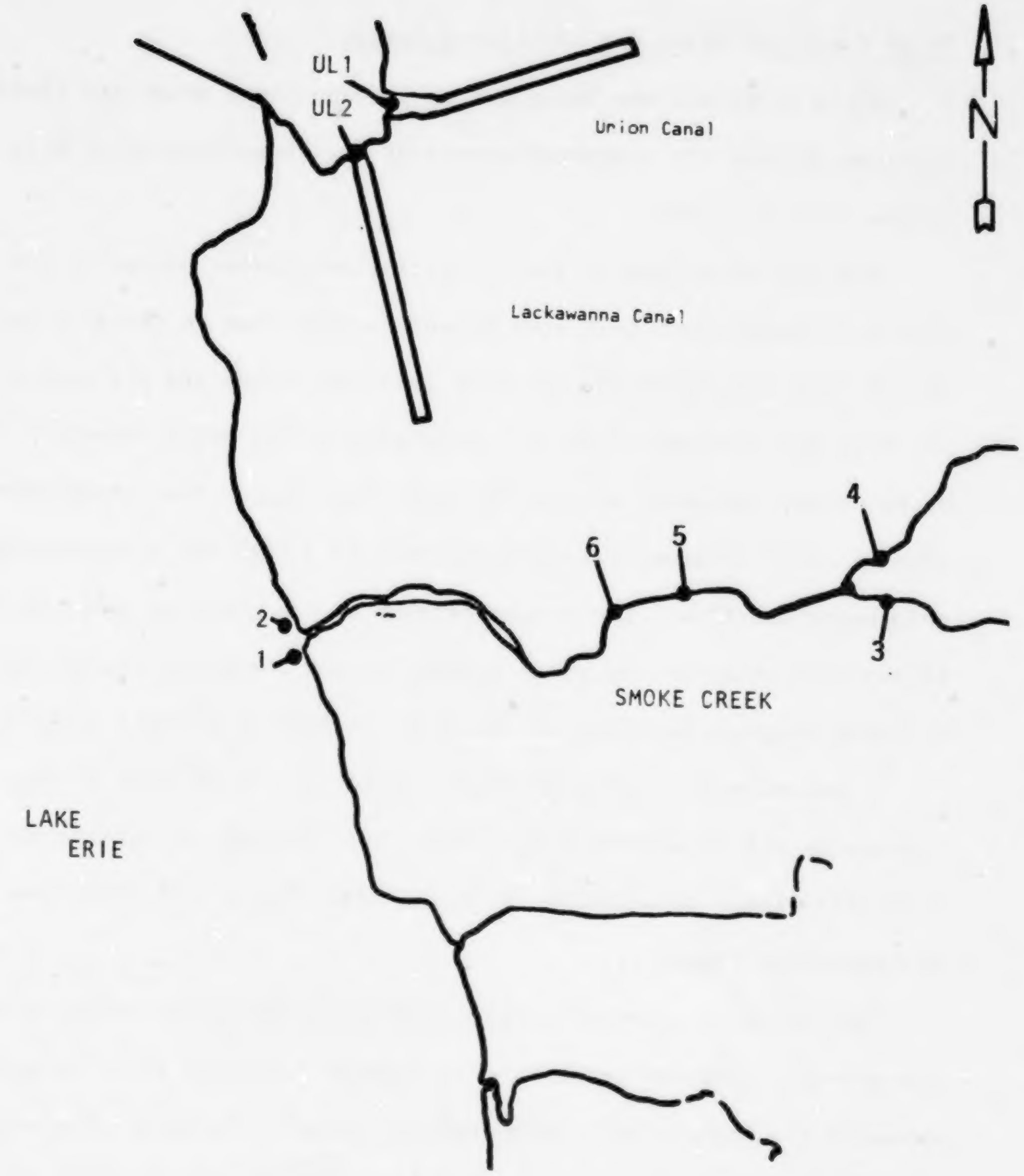

UL1
UL2
Union Canal
N
Lackawanna Canal
4
6
5
2
1
3
SMOKE CREEK
LAKE
ERIE

FIGURE 10: ARTIFICIAL SUBSTRATE SAMPLING SITES AT SMOKE CREEK AND THE UNION AND LACKAWANNA CANALS. DETAILED SITE DESCRIPTION FOR THIS FIGURE IS PRESENTED IN APPENDIX C.

TABLE 8. PAH CONCENTRATIONS IN ARTIFICIAL SUBSTRATES SMOKE CREEK AND UNION AND LACKAWANNA CANALS (ng/SUBSTRATE)

	Total PAH
Site 1	190
Site 2	150
Site 3	330
Site 4	61
Site 5	78
Site 6	56
Site UL1	110
Site UL2	7600

reported from Lake Erie site 1 (Fig. 3). The individual PAH reported in Bethlehem Steel outfalls approximate this increase at Lake Erie from site 1 to site 8 by an approximate four to seven fold increase depending on the individual PAH compound. Sediment samples from the Union and Lackawanna Canals exhibit a marked decrease in total PAH concentration with distance away from the canal entrances (Fig. 4). The sediment PAH composition exhibits relatively high concentrations of fluoranthene, pyrene, chrysene, benzoanthracene, and other PAH compounds also found in water samples from Bethlehem Steel outfalls (Table 2), but compounds such as fluoranthene, pyrene, and chrysene were found in relatively high concentrations in sediment from other locations in the study area. Smoke Creek and Union and Lackawanna sediment sampling locations exhibited an association in the cluster analyses (Fig. 11 - Cluster 2, Table 9). However, the cluster analyses suggest similarities in relative PAH distribution between sites associated with the Bethlehem Steel operation and areas far removed from this location such as Tonawanda Creek, Two Mile Creek, and two locations on the Canadian side of the Niagara River, Frenchman's Creek, and Black Creek (Fig. 11). This may be due to the most common source of PAH contamination, air deposition of products of combustion. Because of the ubiquitous nature of combustive PAH production it is not suprising that diverse areas have similar PAH constituents. Laflamme and Hites (1980) indicate that qualitative and quantitative similarities in PAH compounds in sediments from diverse areas result from combustive processes. It is therefore not unexpected that a steel manufacturing operation employing various combustive processes for manufacturing would have similar PAH composition in its

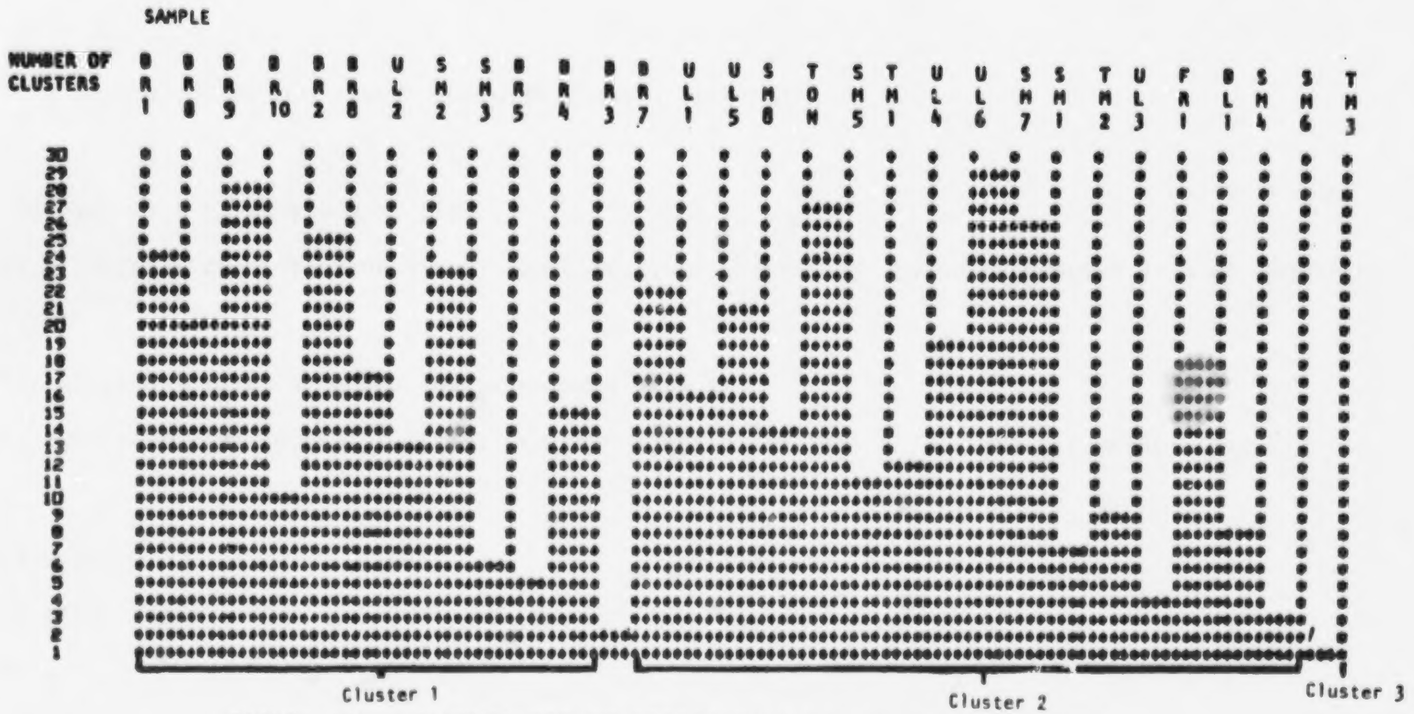


FIGURE 11: CLUSTER MAP OF ASSOCIATION OF SEDIMENT SAMPLING SITES BASED ON THEIR PAH COMPOSITION.

B R 1-10	-	Buffalo River (Fig. 2)
S M 1-8	-	Lake Erie Transect Across the Mouth of Smokes Creek (Fig. 3)
U L 1-6	-	Union and Lackawanna Canals (Fig. 4)
T M 1-3	-	Two Mile Creek 1-3 (Fig. 5)
B L 1	-	Black Creek Mouth at Niagara River
F R 1	-	Frenchmans Creek Mouth at Niagara River
Ton	-	Tonawanda Creek Mouth at Niagara River

TABLE 9. PAH PERCENT COMPOSITION OF CLUSTERS FROM CLUSTER MAP OF SITE ASSOCIATION

	Percent of Each PAH				
	Benzo(e)pyrene	Chrysene	Perylene	Benzo(a)pyrene	Dibenzo(a,h)anthracene
Cluster 1	15	9	58	13	5
Cluster 2	21	17	36	21	5
Cluster 3	80	2	0	13	5
Buffalo River 3 & 4	9	4	79	6	2
Buffalo River 5	8	4	56	8	26

Cluster 1 includes the following sites: Buffalo River Sites 1-6, 8-10 (Fig. 2), Smoke Creek Transect Sites 2-3 (Fig. 3),Union and Lackawanna Site 2.

Cluster 2 includes the following sites: Buffalo River 7 (Fig. 2), Union-Lackawanna 1, 3-6, Smoke Creek 1, 4-8 (Fig. 3), Two Mile Creek 1 and 2 (Fig. 5).

Cluster 3 is made up of one site: Two Mile Creek 3 (Fig. 5).

immediate area to distant areas presumably receiving PAH contamination from other combustion sources. Heit et al., 1980 report high concentrations of fluoranthene, pyrene, and a number of other PAH compounds from upper sediments (0-4 cm) of Adirondack Lakes without nearby sources of PAH which they attribute to combustive sources. The proportional and actual concentrations of these PAH compounds decrease markedly in deep sediments with the exception of perylene which has been attributed to natural sources.

Two Mile Creek

Three artificial substrates were placed in Two Mile Creek (Fig. 12). PAH concentrations in artificial substrates are presented in Table 11. All substrates analyzed accumulated PAH, however concentrations of PAH were considerably higher at the mouth of Two Mile Creek than at the other two locations (Table 10).

Although artificial substrate sampling suggested that the highest concentrations of PAH were at the mouth of Two Mile Creek, field investigation suggested that a source of PAH might be upstream. PAH contaminated sediment from upstream could settle near the mouth and subsequent leaching from these contaminated sediments may have produced the high PAH concentrations in the artificial substrate. Further field inspections resulted in the discovery of an oil containment boom at an intermittent tributary of Two Mile Creek which entered the creek approximtely 1/2 mile from its junction with the Niagara River. Substrates downstream from this intermittent tributary and upstream from the junction of this tributary had medium high and high concentrations of PAH respectively. A second substrate sampling was done. Artificial

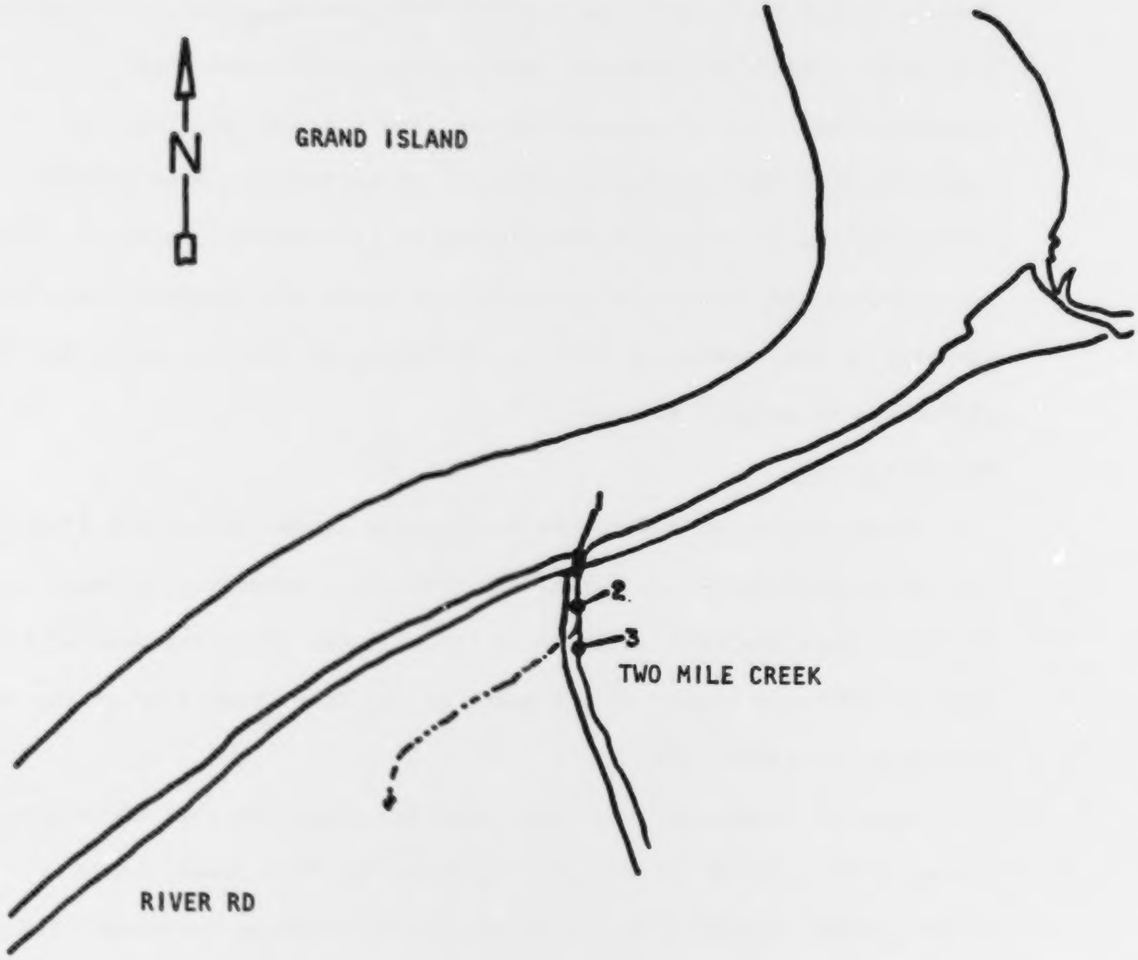

N
GRAND ISLAND
2
3
TWO MILE CREEK
RIVER RD

FIGURE 12: TWO MILE CREEK ARTIFICIAL SUBSTRATE SAMPLING SITES DETAILED SITE DESCRIPTION FOR THIS FIGURE IS PRESENTED IN APPENDIX C.

TABLE 10. PAH CONCENTRATIONS IN ARTIFICIAL SUBSTRATES FROM TWO MILE CREEK (ng/substrate)

		Phenanth.	Anthracene	Fluoranth.	MePhenanth.	MeAnth.	Benzofluor.	Benzanth.	Chrysene	Benz(e)pyr.	Perylene	Benz(a)pyr.	Dibenz(a,h)	Total PAH
Site 1	a	240	50	950	210	170	260	460	600	500	460	380	160	440
Site 2	b	20	3.0	70	14	12	17	29	44	38	35	31	21	330
Site 3	b	19	4.3	92	20	15	23	27	61	47	40	38	22	408

substrates were placed directly in the intermittent tributary immediately downstream from the oil boom. Two other substrates were placed in Two Mile Creek immediately upstream and downstream from the intermittent tributary. The substrate in the intermittent tributary exhibited the highest PAH accumulation, while the substrate upstream from the junction of the intermediate tributary exhibited a moderate PAH accumulation and the downstream substrate exhibited the lowest PAH accumulation.

Sediment from different sites in the Two Mile Creek drainage did not appear to be similar in their relative PAH compound composition. At Site 3 (Fig. 5, Table 11) which was the furthest upstream in the intermittent tributary, the more soluble PAH compounds such as fluoranthene, pyrene, phenanthrene, and methyl phenanthrene were in a greater proportion to less soluble compounds than when compared to Site 1 (Fig. 5, Table 11) at the mouth of Two Mile Creek. However, benzofluorene, which has a relatively low solubility (Mackay and Yinz Shiu, 1977), is in relatively high concentrations at both sites 1 and 3. At site 1 perylene, benzo(e)pyrene, benzo(a)pyrene, chrysene and other similar low solubility PAH compound comprise most of the total PAH composition (Table 11, Fig. 5). Because of the intermittent nature of the tributary at site 3 the more soluble PAH may tend to remain in the sediment while at site 1 the more soluble PAH are subject to constant leaching.

The presence of petroleum storage facilities in the uppermost sections of the intermittent tributary to Two Mile Creek with a history of 12 petroleum spills to this drainage since 1976 (NYS DEC records) suggest that this is a source of PAH pollution to Two Mile Creek. Although an attempt was made to compare PAH patterns in Two Mile Creek

TABLE 11. PAH SEDIMENT CONCENTRATION FROM TWO MILE CREEK (ORGANIC WEIGHT ng/mg)

COMPOUND	CONCENTRATION Site 1 River Rd. Bridge	 Site 3 Intermittent Tributary
FLUORENE	ND*	13
PHENANTHRENE	5	65
ANTHRACENE	ND	17
FLUORANTHENE	66	260
MePHENANTHRENE	2	34
PYRENE	11	760
MeANTHRACENE	2	45
BENZOFLUORENE	81	200
BENZANTHRACENE	49	21
CHRYSENE	51	1
BENZO(e)PYRENE	51	46
PERYLENE	120	ND
BENZO(b)FLUORANTHENE	61	7
BENZO(k)FLUORANTHENE	30	3
BENZO(a)PYRENE	61	4
DIBENZ(a,h)ANTHRACENE	30	1
BENZO(g,h,i)PERYLENE	52	5
INDENO(1,2,3-c,d)PYRENE	56	4
TOTAL	730	1500

*ND - Not Detected

with known PAH patterns in various petroleum products, Neff (1979) indicates that a high degree of variability exists in the PAH composition of these products. This variability prevents a comparison of PAH distributions in a contaminated area with a given petroleum product. In addition, the physical, chemical, and biological processes acting upon PAH in the aquatic environment as described by Herbes et al. (1980) can alter the relative composition of PAH compounds in the aquatic environment substantially.

Artificial substrate sampling in Two Mile Creek showed remarkably similar PAH compositions (Fig. 13, Table 11), with the highest concentration in substrates at the mouth of Two Mile Creek. The relatively high PAH accumulation of a substrate placed upstream from the junction of Two Mile Creek and the intermittent tributary suggested another upstream source of PAH in addition to the sources associated with the intermittent tributary. Sediments from four storm sewers entering Two Mile Creek between Sheridan Drive and the Youngman Expressway, approximately 1.5 miles upstream from the junction of Two Mile Creek and the intermittent tributary identified as having one source of PAH pollution, were sampled in 1982 by DEC. Acenaphthene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)fluoranthene, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, napthalene, phenanthrene and pyrene were present at concentrations of less than or equal to 2-8.7 ug/gm dry weight. Eight of the PAH compounds present were at concentrations over 2 ug/gm. The following PAH compounds were quantified on a dry weight basis:Anthracene (8 ug/gm), Benzo(a)anthracene (2.4 ug/gm), Benzo(a)pyrene (2.5 ug/gm), Chrysene (3.5 ug/gm), and Pyrene (8.7 ug/gm).

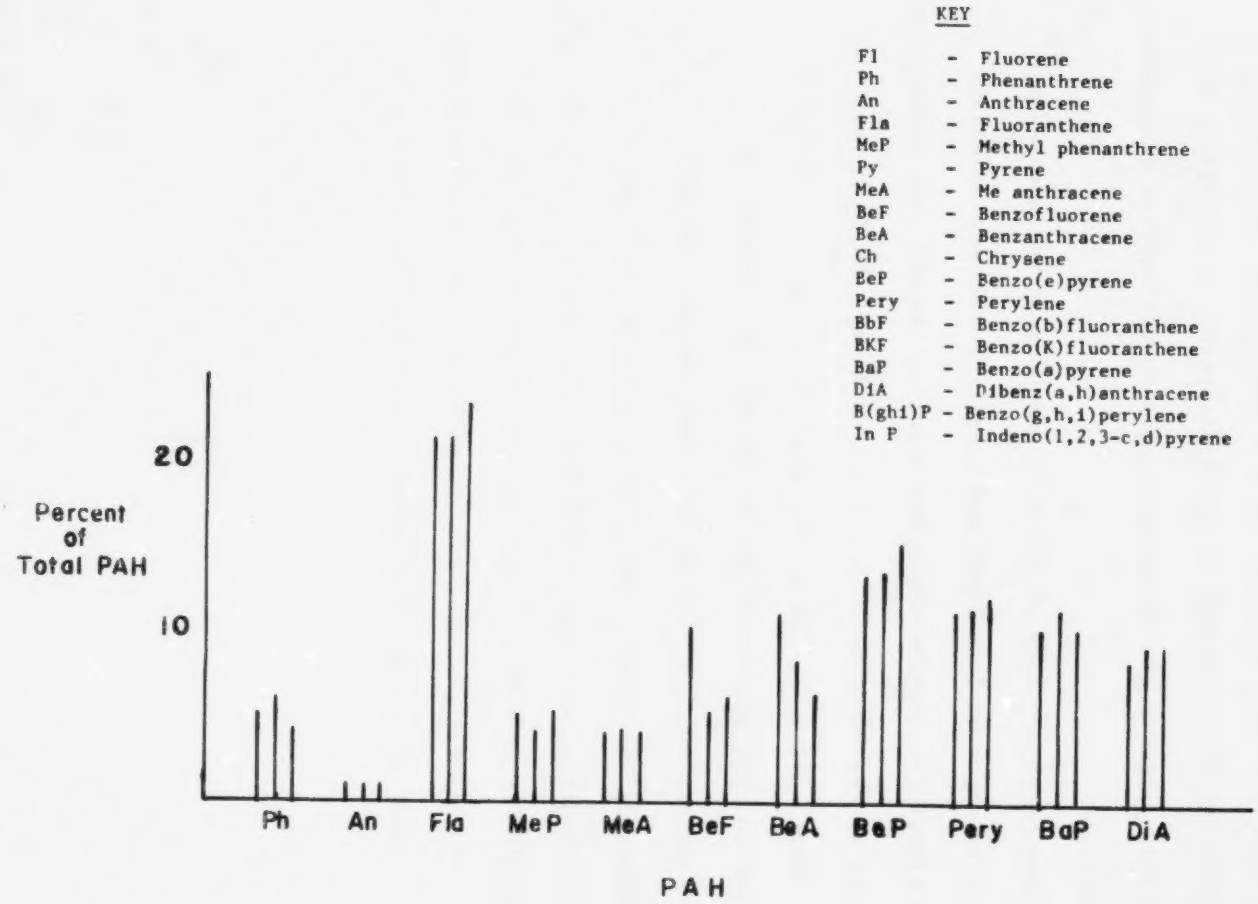


FIGURE 13: PERCENT COMPOSITION OF TOTAL PAH IN TWO MILE CREEK ARTIFICIAL SUBSTRATES SITES 1, 2, AND 3 (FIG. 12). FIRST, SECOND, AND THIRD LINES ARE SITES 1, 2, AND 3 RESPECTIVELY.

Fluorene and phenanthrene were not detected in sediments from the mouth of Two Mile Creek. However, the remainder of the compounds quantified in the storm sewer sediment were at concentrations within the same order of magnitude as those occurring in sediments at the mouth of Two Mile Creek. The PAH contamination identified in the storm sewers may represent another significant source of PAH to Two Mile Creek. Storm sewers have been identified as routes of PAH contamination to the aquatic environment (Herman, 1981).

Comparison of proportions of PAH compound composition among 2 Two Mile Creek sites and a Buffalo River and Lake Erie sediment sampling sites which apparently receive their PAH input ultimately from combustive sources reveal differences in their PAH composition. Two Mile Creek sediment at Site 3 (Fig. 14, Table 11), which is probably receiving its PAH contamination from petroleum spills, exhibits a substantial percentage of pyrene which is 51% of the total PAH at this site. Perylene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, and indeno(1,2,3,c,d)pyrene are at extremely low relative concentrations, or not present at this location as compared to the Buffalo River and Lake Erie, which have PAH contamination which is presumably derived from combustive sources.

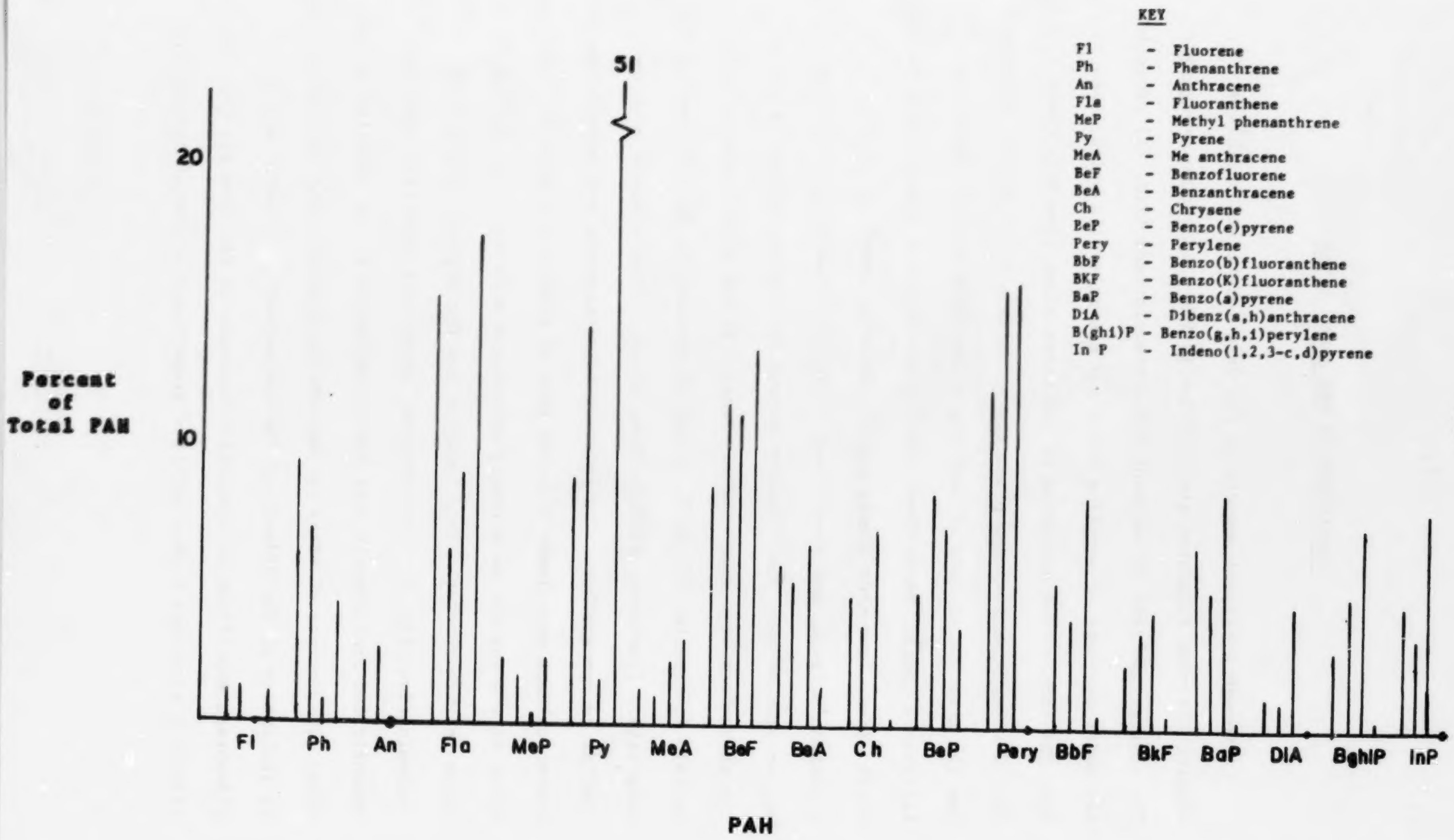


FIGURE 14: PERCENT COMPOSITION OF TOTAL PAH COMPOUNDS IN SEDIMENT. THE FOUR LOCATIONS IN EACH GROUP ARE SMOKE CREEK TRANSECT SITE 8 (FIG. 3), BUFFALO RIVER SITE 6 (FIG. 2), TWO MILE CREEK SITE 1 (FIG. 5), AND TWO MILE CREEK SITE 3 (FIG. 5) RESPECTIVELY.

COMPARISON OF PAH AMONG SITES

Although localized sources of PAH were identified in this study, cluster analyses suggested similarities in PAH composition among sites. The cluster analysis of sediment PAH concentrations (Fig. 11) produced two major clusters of sampling sites and a single site which appeared to have PAH composition unrelated to the other sites (Two Mile Creek 3, Fig. 5). Cluster 1 is composed primarily of Buffalo River sites. Cluster 2 has the greatest variety of sampling sites which include Union and Lackawanna Canals, Smoke Creek mouth transect sites (Lake Erie), Two Mile Creek sites, Tonawanda Creek, and two Canadian sampling sites , Frenchman's Creek, and Black Creek. Cluster 1 had relatively high percentages of perylene. Benzo(e)pyrene and benzo(a)pyrene relative concentrations were approximately equal. Within this cluster, three Buffalo River sites (Sites 3, 4, and 5) appeared to be different in PAH composition from other Buffalo River sites. Sites 3 and 4 were most similar to one another. The relative benzo(a)pyrene and benzo(e)pyrene concentrations were lower than the mean of cluster 1 (Table 9). Buffalo River Site 5 was not as strongly associated with any other Buffalo River sites in this cluster. This location had the highest sediment PAH contamination (Fig. 2). Furthermore, artificial substrate sampling demonstrated consistently high PAH accumulation in the vicinity of this site. The variety of sites having similar distributions in cluster 2 may be indicative of the widespread PAH contamination of water due to widespread deposition of combustive products of PAH from air into water. Cluster 2 sites had higher relative proportions of benzo(e)pyrene and benzo(a)pyrene and almost twice the proportion of chrysene in cluster 1 sites. These types of PAH compounds are characteristic contaminants associated with iron and steel manufacturing operations. This type of industry is associated with some of the sites located in cluster 2. The Two Mile Creek site 3 appears to have a unique PAH composition based on the cluster analysis. Extremely high proportions of benzo(e)pyrene were present in sediment at this location and no perylene was detected in sediment at this site. Perylene was at the highest concentration of the five PAH compounds in the other two clusters. This location was the only site that had high PAH contamination which could be attributed to oil pollution.

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

Artificial substrates were useful tools for identifying areas of PAH input in the study area. Furthermore, once an area was identified by these substrates as having PAH contamination, substrates could be used to further isolate the input area of PAH. It is deemed significant that areas identified as having PAH contamination by artificial substrates generally had high PAH concentrations in sediment.

The Buffalo River and the aquatic environment surrounding the Bethlehem Steel property are grossly contaminated by PAH compounds. A major input area of PAH in the Buffalo River is in the area of the South Park Bridge. Discharge sampling identified elevated PAH levels in one Buffalo Color discharge; however, other sources of PAH may occur in this area. It is possible that the PAH accumulated by artificial substrates came from contaminanted sediment leaching PAH into the water column. Therefore, contaminated sediment cannot be eliminated as a source to the water column. It is clear from discharge sampling that Bethlehem Steel is a source of PAH to Smoke Creek. The increase in sediment PAH levels in Lake Erie from south to north paralleling the Bethlehem Steel property and the high degree of sediment PAH contamination in the Union and Lackawanna Canals point to Bethlehem Steel as the source of PAH contamination in this area.

The PAH contamination of Two Mile Creek is likely to be high because it is a small body of water with at least two sources of PAH. It is apparent that the petroleum storage facilities present a continuing PAH input to this creek. A second input to this drainage appears to be storm sewers in Two Mile Creek upstream from the area contaminated by petroleum spills.

The Buffalo Sewer Authority is a source of PAH to the Niagara River but the magnitude of PAH input appears to be small. However, in a facility of this type it is expected that PAH discharges may vary considerably due to the variety of municipal, commercial, and storm sewer discharges to the Buffalo Sewer Authority.

Superimposed upon the specific areas of high PAH contamination is a generalized PAH contamination of the study area.

RECOMMENDATIONS

The sources of PAH in the Buffalo River require further verification. The Buffalo Color and Allied Chemical discharges should be resampled to confirm the identified discharge of PAH from the Buffalo Color outfall and eliminate the other outfalls as sources of PAH. The major source of PAH to the Buffalo River water may be from previously contaminated sediments. If ongoing discharges are not the primary PAH source then a study to identify the impact of transfer to the water column upon biota should be initiated.

A PAH monitoring program is recommended for the area surrounding Bethlehem Steel. Operations at this facility have been greatly reduced and therefore PAH levels should drop. Monitoring should be done to test this hypothesis.

The oil storage facilities at the upstream area of the intermittent tributary to Two Mile Creek should better contain their spillage. The sources of PAH found in the storm sewers discharging to Two Mile Creek should be identified.

The PAH input to the Niagara River from the Buffalo Sewer Authority requires further investigation. Water and artificial substrate sampling were not done at the same time and consequently the concentrations of PAH in water leading to accumulations in artificial substrates may have been considerably higher than those that were measured in the water sample. If PAH concentrations in the Buffalo Sewer Authority discharge are found to be high upon repetitive sampling then the sources of those inputs to the Authority should be identified.

LITERATURE CITED

Basu, D. K. and J. Saxena. 1978. J. Environ. Sci and Technol. 12. 795-798.

Baum, E. J. 1978. Polycyclic Aromatic Hydrocarbons and Cancer Vol. 1. Gelboin and Ts'o Eds. Academic Press. pp. 45-70.

Black, J. J. 1983. Epidermal hyperplasia and neoplasia in brown bullheads *Ictalurus nebulosus* in response to repeated application of PAH contaminated extract of polluted river sediment in Polynuclear Aromatic Hydrocarbons: Formation Metabolism and Measurements. Battelle Press, Columbus. pp. 99-111.

Calocerinos and Spina Consulting Engineers 1982. Buffalo River Combined Sewer Overflow Study. Interim Report on Water Quality. 47 pp.

Dunn, B. P. 1979. In Polynuclear Aromatic Hydrocarbons: Chemistry and Biological Effects; Biorseth, A., and A. J. Dennis, Eds. Columbus, p. 367-377.

Eadie, B. J., W. Faust, W. S. Gardner and T. Nalepa. 1982. Chemosph. 11 (2): 185-191.

Heit, M., Y. Tam, C. Klusek and J. C. Burke. 1981. Water, Air, and Soil Pollution 15, 441-464.

Herbes, S. E., G. R. Southworth, D. L. Schaeffer, W. L. Griest, and M. P. Moskarinec. 1980. The Scientific Basis of Toxicity Assessment. H. Witschi Ed. Elsevier/North Holland Biomedical Press.

Herman, R. 1981. Water, Air, and Soil Pollution 16, 445-467.

Lao, R. C., R. S. Thomas and J. L. Monkman (1975). J. Chromatog. 112: 681-700. in Neff. J. M. 1979. Polycyclic Aromatic Hydrocarbons in the Aquatic Environment: Sources, Fates, and Biological Effects. Applied Science Publishers LTD. London. 262 pp.

Laflamme, R. E. and R. A. Hites 1978. Geochimica et Cosmochimica Acta. 42, 289-303.

Mackay, D. and W. Y. Shiu. 1977. J. Chem. and Engr. Data. 22(4), 399-402.

Neff, J. M. 1979. Polycyclic Aromatic Hydrocarbons in the Aquatic Environment: Sources, Fates, and Biological Effects. Applied Science Publishers Ltd. London. 262 pp.

SAS 1979. SAS Users Guide. Helwig and Council Eds. SAS Institute. North Carolina. 494 pp.

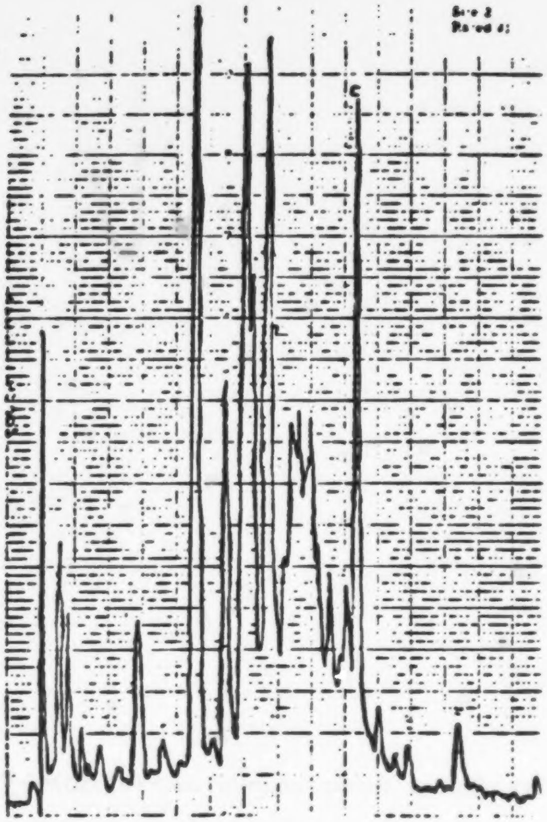
Schimberg, R. W., P. Pfaffli, and A. Tossavainen, 1980. J. Toxicol. and Environ. Hlth. 6, (5-6), 1187-1194.

USEPA. 1980. Ambient Water Quality Criteria for Polynuclear Aromatic Hydrocarbons. EPA 440/5-80-069.USEPA. 1979. Treatability Manual. Vol I. Treatability Data.

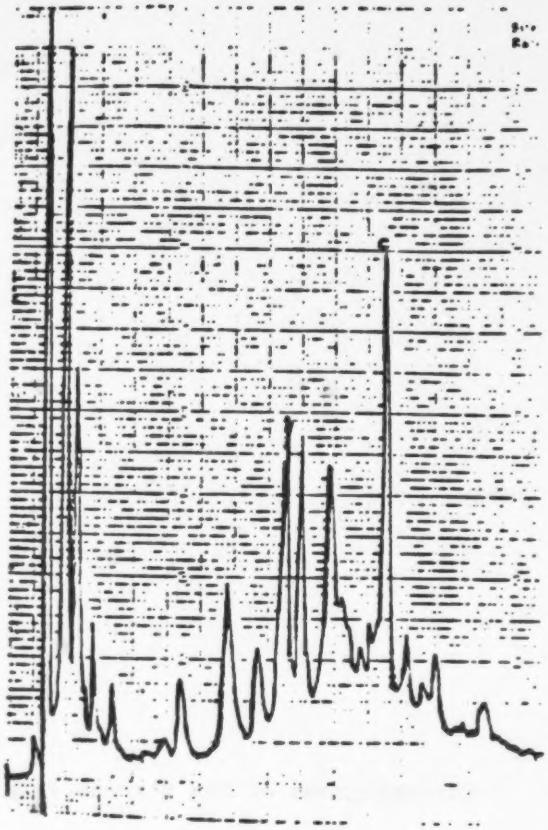
Wong, J. 1981. Persistent Toxic Substances in Runoff from the City of Cornwall. 1978 Canada-U.S. Great Lakes Water Quality Agreement Project No. 1502.

APPENDIX A

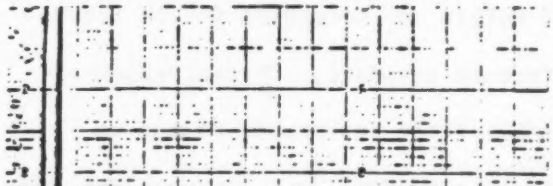
Chromatograms of PAH Screens from Artificial Substrates from Preliminary Survey. (The region of the chromatogram that reflects the presence of PAH starts about 1 cm from the left margin and continues to the right. The peak marked C is a chrysene reference standard. Chromatograms are presented in order of decreasing rank. Sites correspond to map of preliminary survey locations on fig. 1)



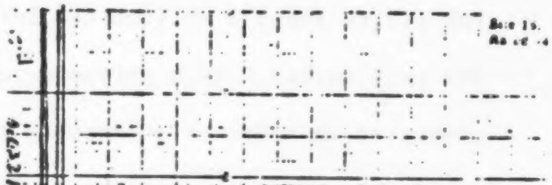
Site 2 - Rated #1



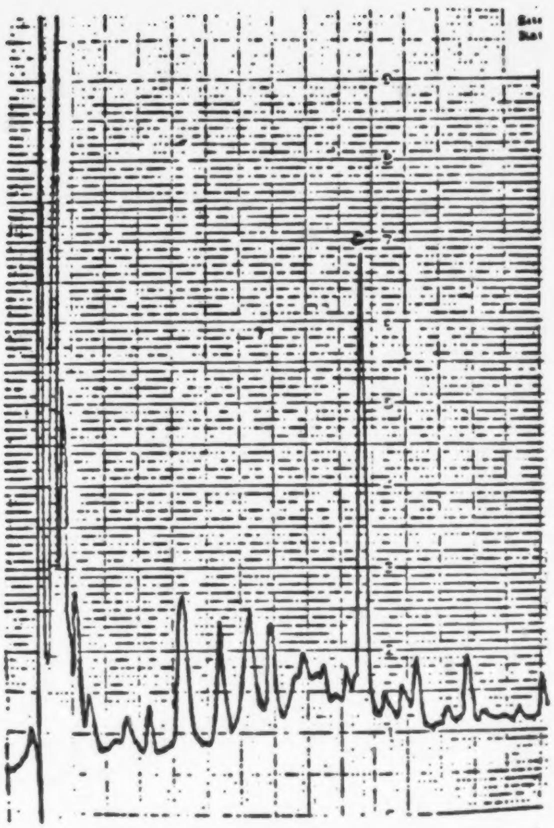
Site 1 - Rated #2



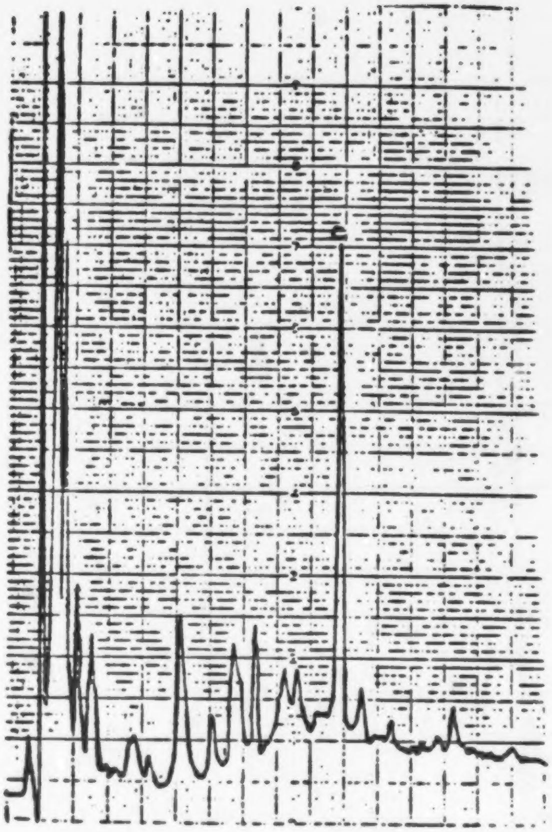
Site 2 - Rated #3



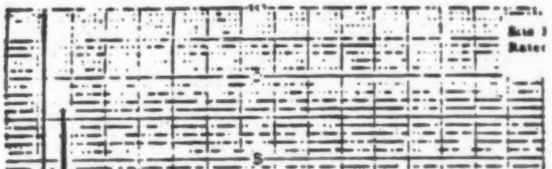
Site 15 - Rated #4



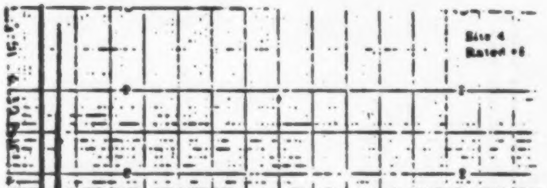
Site 9 - Rated #5



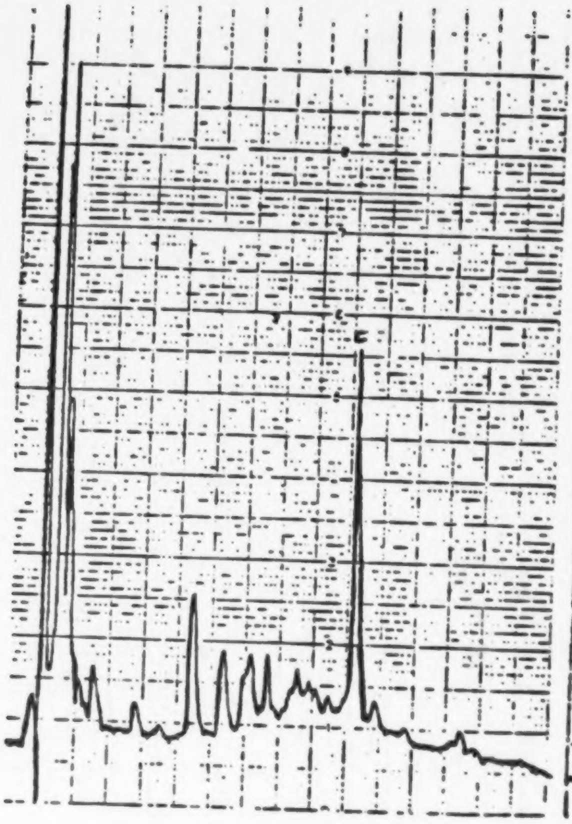
Site 1 - Rated #6



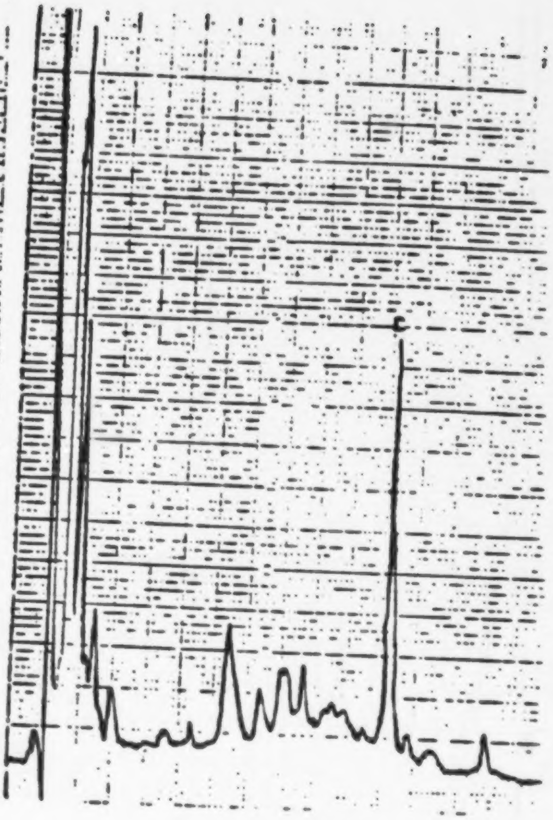
Site 10 - Rated #7



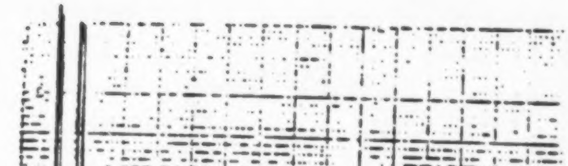
Site 4 - Rated #8



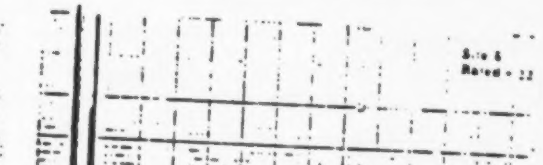
Site 4 - Rated #9



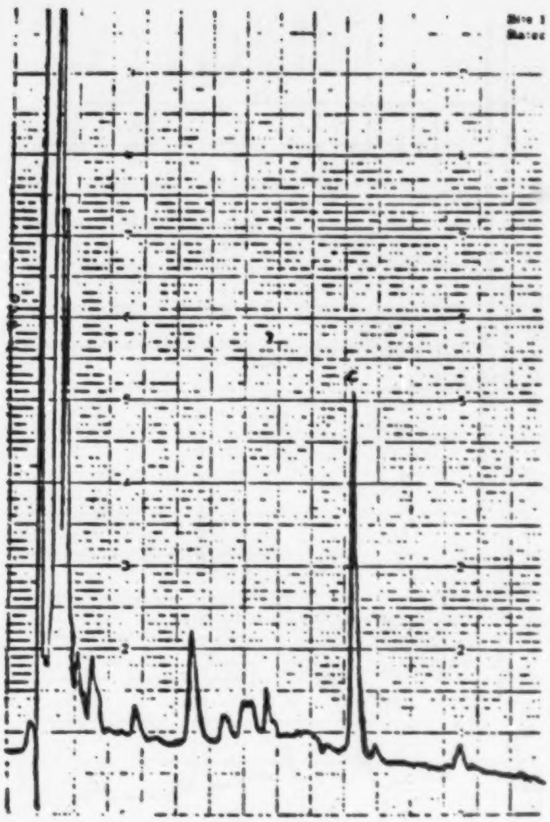
Site 11 - Rated #10



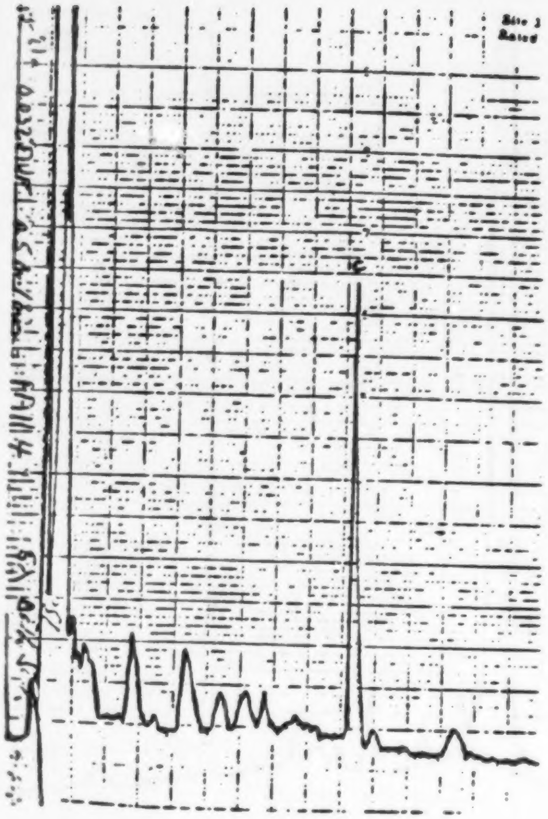
Site 12 - Rated #11



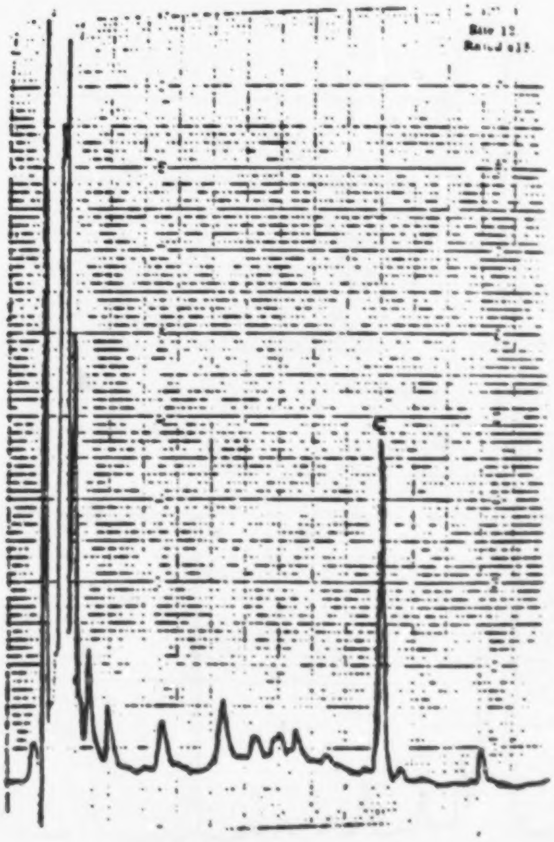
Site 8 - Rated #12



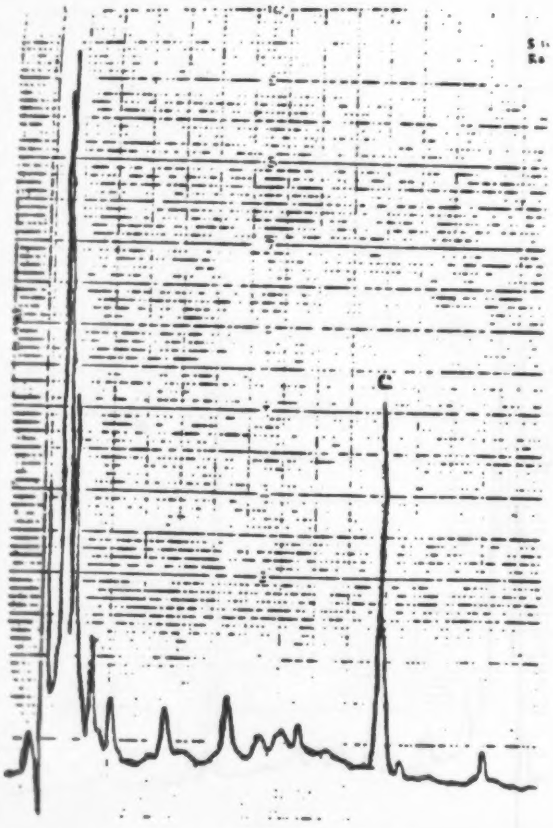
Site 16 - Rated #13



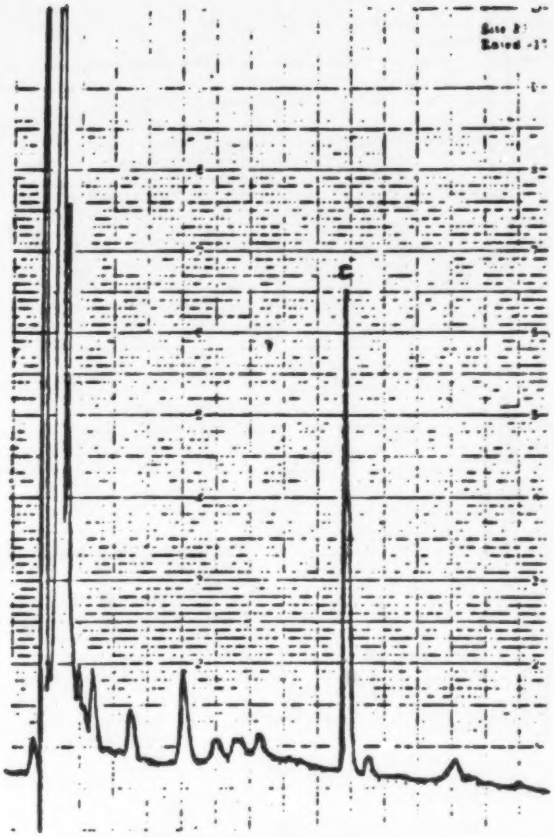
Site #3 - Rated #14



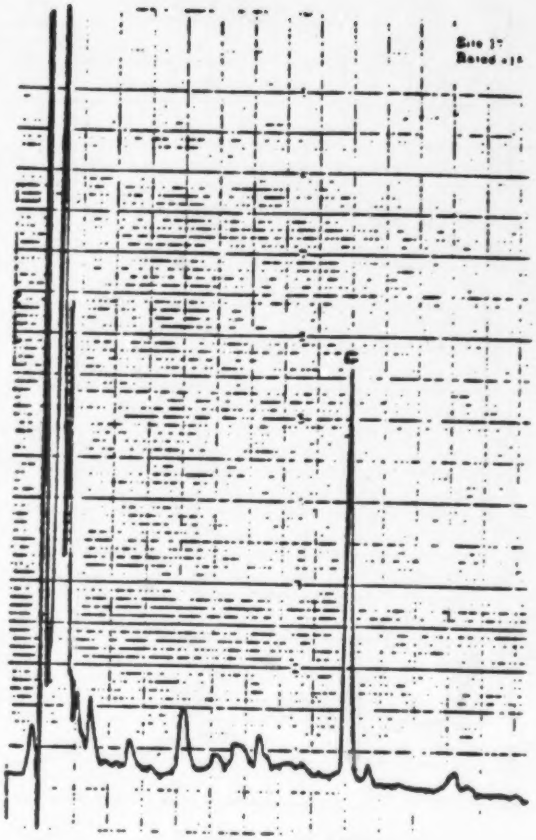
Site 13 - Rated #15



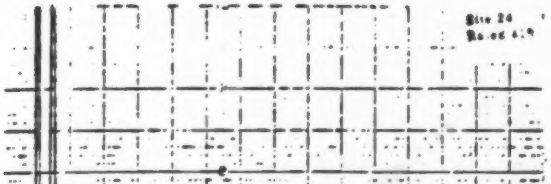
Site 14 - Rated #16



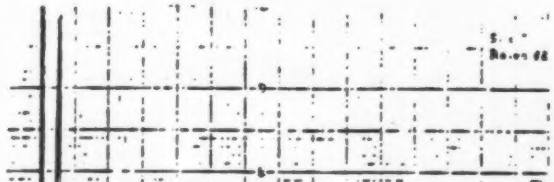
Site 23 - Rated #17



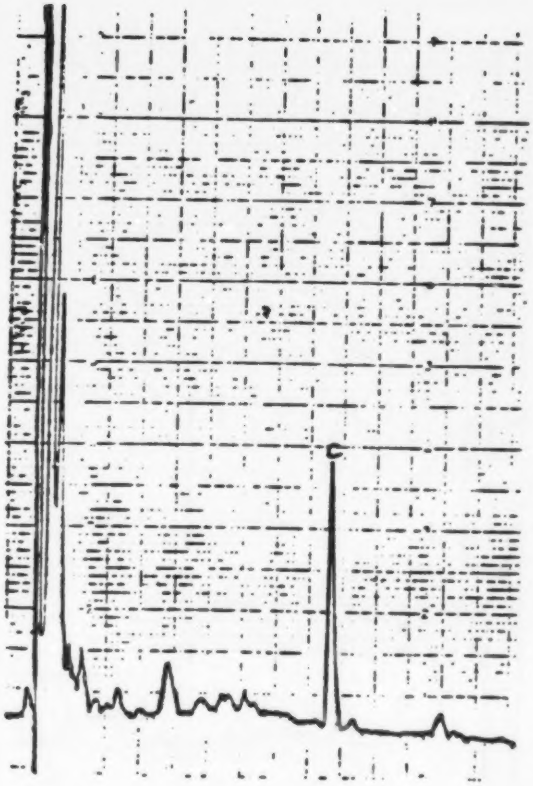
Site 17 - Rated #18



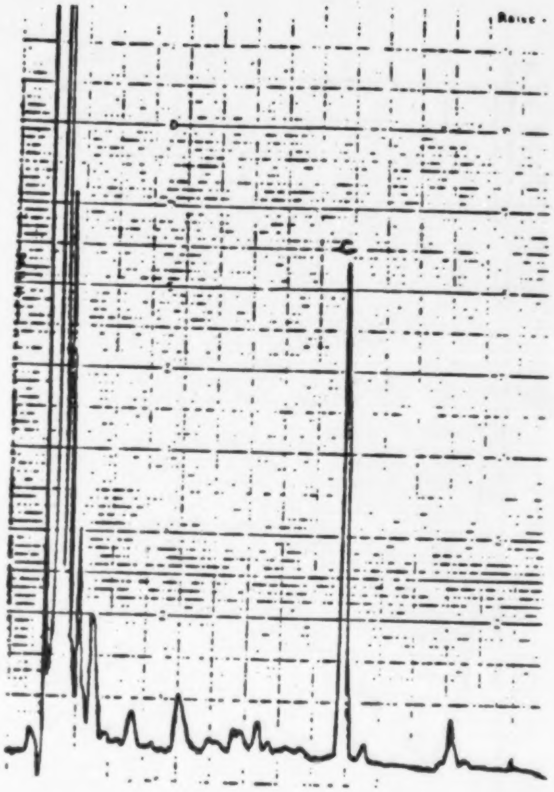
Site 24 - Rated #19



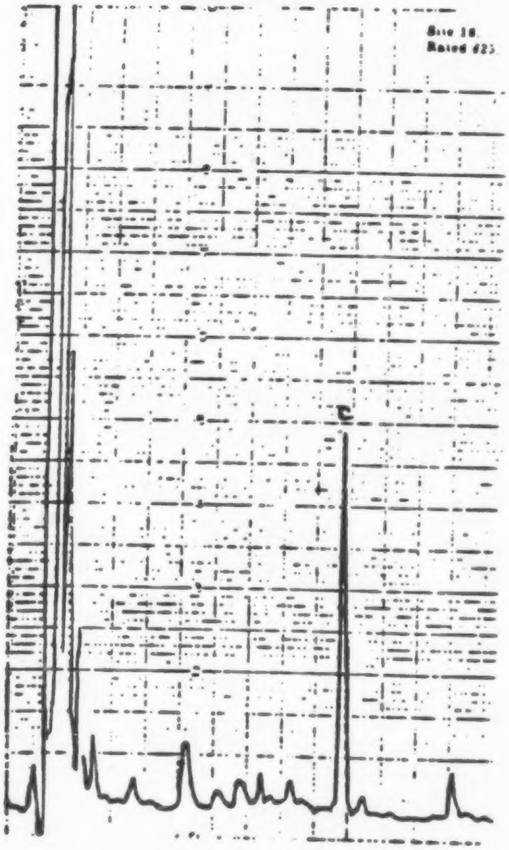
Site #7 - Rated #20



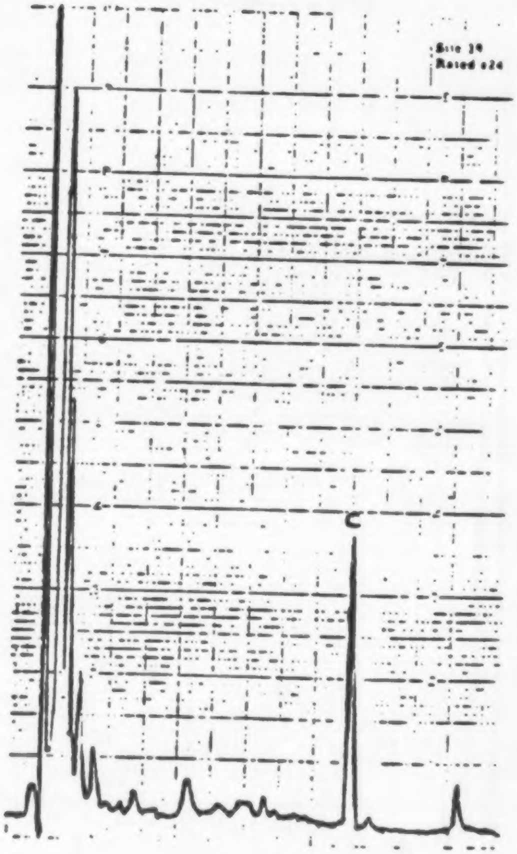
Site 22 - Rated #21



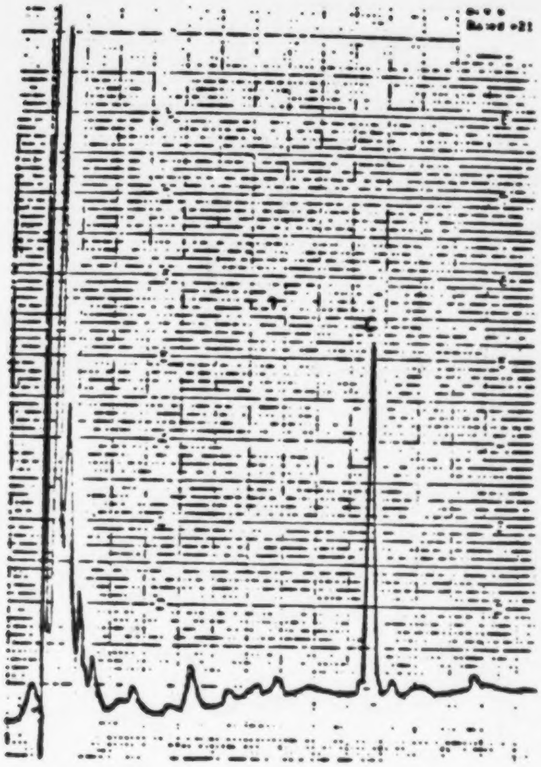
Site 20 - Rated #22



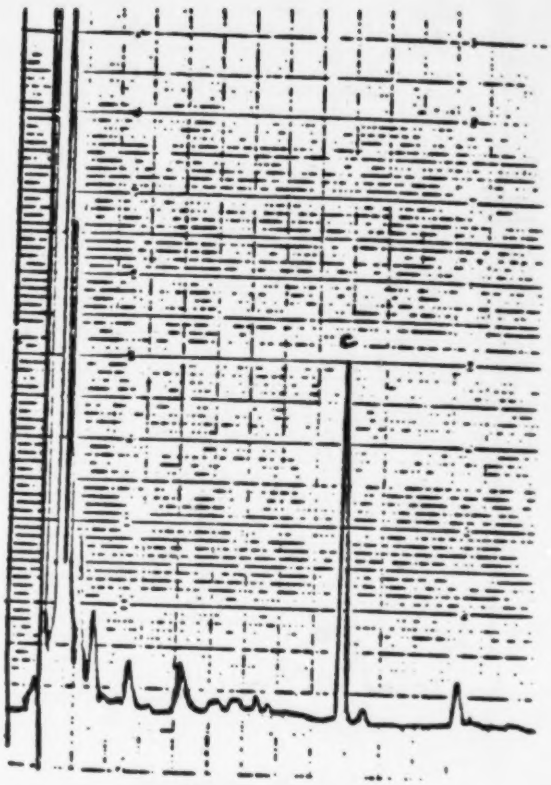
Site 18 - Rated #23



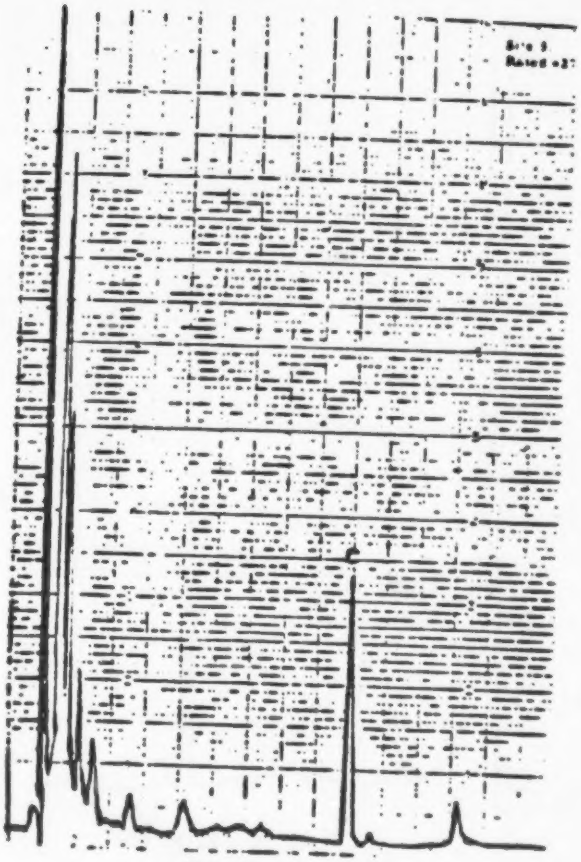
Site 19 - Rated #24



Site 8 - Rated #25



Site 6 - Rated #26



Site 5 - Rated #27

APPENDIX B

PAH Sediment Concentrations for All Sampling Sites (site locations correspond to sediment sampling sites in text for Buffalo River, Smoke Creek Transect in Lake Erie, Union and Lackawanna Canals, and Two Mile Creek)

TABLE 1. BUFFALO RIVER: SITE 1. BUFFALO RIVER DOWNSTREAM FROM CONFLUENCE OF NORTH AND SOUTH BRANCHES. PAH SEDIMENT CONCENTRATIONS

	CONCENTRATIONS		
COMPOUND	WET ng/gm	DRY ng/gm	ORGANIC ng/mg
FLUORENE	ND*	ND	ND
PHENANTHRENE	380	760	20
ANTHRACENE	100	190	5
FLUORANTHENE	1700	3400	86
MePHENANTHRENE	150	300	7
PYRENE	1000	2000	51
MeANTHRACENE	ND	ND	ND
BENZOFLUORENE	400	800	20
BENZANTHRACENE	300	600	15
CHRYSENE	250	500	13
BENZO(e)PYRENE	940	1800	48
PERYLENE	1300	2500	64
BENZO(b)FLUORANTHENE	470	940	24
BENZO(k)FLUORANTHENE	200	400	10
BENZO(a)PYRENE	320	630	16
DIBENZ(a,h)ANTHRACENE	84	170	4
BENZO(g,h,i)PERYLENE	380	750	19
INDENO(1,2,3-c,d)PYRENE	410	800	21
TOTAL	8400	16500	420

*ND - Not Detected

TABLE 1 CONT'D. SITE 2. BUFFALO RIVER AT DOWNSTREAM BOUNDARY OF MOBIL TANK FARM. PAH SEDIMENT CONCENTRATIONS

	CONCENTRATIONS		
COMPOUND	WET ng/gm	DRY ng/gm	ORGANIC ng/mg
FLUORENE	73	170	3
PHENANTHRENE	360	840	14
ANTHRACENE	73	170	3
FLUORANTHENE	1400	3300	56
MePHENANTHRENE	150	350	6
PYRENE	740	1700	29
MeANTHRACENE	100	240	4
BENZOFLUORENE	520	1200	21
BENZANTHRACENE	270	640	11
CHRYSENE	150	360	6
BENZO(e)PYRENE	360	850	14
PERYLENE	890	2100	35
BENZO(b)FLUORANTHENE	370	860	15
BENZO(k)FLUORANTHENE	170	400	7
BENZO(a)PYRENE	290	670	11
DIBENZ(a,h)ANTHRACENE	60	150	2
BENZO(g,h,i)PERYLENE	270	640	11
INDENO(1,2,3-c,d)PYRENE	260	620	10
TOTAL	6500	15000	260

TABLE 1 CONT'D. SITE 3. BUFFALO RIVER 200 YDS. UPSTREAM OF SOUTH PARK BRIDGE. PAH SEDIMENT CONCENTRATIONS.

	CONCENTRATIONS		
COMPOUND	WET ng/gm	DRY ng/gm	ORGANIC ng/mg
FLUORENE	61	130	2
PHENANTHRENE	330	700	13
ANTHRACENE	99	210	3
FLUORANTHENE	1200	2500	46
MePHENANTHRENE	160	350	6
PYRENE	660	1400	26
MeANTHRACENE	110	240	4
BENZOFLUORENE	600	1300	24
BENZANTHRACENE	220	460	8
CHRYSENE	110	240	4
BENZO(e)PYRENE	1300	2800	52
PERYLENE	2400	5100	95
BENZO(b)FLUORANTHENE	310	660	12
BENZO(k)FLUORANTHENE	150	320	6
BENZO(a)PYRENE	220	470	9
DIBENZ(a,h)ANTHRACENE	57	120	2
BENZO(g,h,i)PERYLENE	340	720	13
INDENO(1,2,3-c,d)PYRENE	420	890	17
TOTAL	8700	1900	340

TABLE 1 CONT'D. SITE 4. BUFFALO RIVER AT SOUTH PARK BRIDGE. PAH SEDIMENT CONCENTRATIONS

COMPOUND	CONCENTRATIONS		
	WET ng/gm	DRY ng/gm	ORGANIC ng/mg
FLUORENE	ND*	ND	ND
PHENANTHRENE	980	2300	43
ANTHRACENE	250	500	11
FLUORANTHENE	1700	4000	76
MePHENANTHRENE	230	520	10
PYRENE	2400	5500	100
MeANTHRACENE	180	400	8
BENZOFLUORENE	1500	3500	66
BENZANTHRACENE	340	790	14
CHRYSENE	150	340	7
BENZO(e)PYRENE	1900	4500	84
PERYLENE	2100	4800	91
BENZO(b)FLUORANTHENE	2400	5500	100
BENZO(k)FLUORANTHENE	290	660	12
BENZO(a)PYRENE	94	220	4
DIBENZ(a,h)ANTHRACENE	61	140	3
BENZO(g,h,i)PERYLENE	92	210	4
INDENO(1,2,3-c,d)PYRENE	880	2000	39
TOTAL	15600	36000	670

*ND - Not Detected

TABLE 1. SITE 5. BUFFALO RIVER AT BUFFALO COLOR. PAH SEDIMENT CONCENTRATIONS

COMPOUND	CONCENTRATIONS		
	WET ng/gm	DRY ng/gm	ORGANIC ng/mg
FLUORENE	330	640	13
PHENANTHRENE	5000	9600	200
ANTHRACENE	1800	3400	70
FLUORANTHENE	5200	10000	210
MePHENANTHRENE	740	1400	29
PYRENE	11000	22000	450
MeANTHRACENE	520	1000	20
BENZOFLUORENE	4800	9200	190
BENZANTHRACENE	1100	2100	42
CHRYSENE	200	390	7
BENZO(e)PYRENE	ND*	ND	ND
PERYLENE	7100	14000	280
BENZO(b)FLUORANTHENE	ND	ND	ND
BENZO(k)FLUORANTHENE	460	900	18
BENZO(a)PYRENE	990	1900	39
DIBENZ(a,h)ANTHRACENE	3300	6300	130
BENZO(g,h,i)PERYLENE	1100	2100	14
INDENO(1,2,3-c,d)PYRENE	410	800	16
TOTAL	44000	86000	1700

*ND - Not Detected

TABLE 1 CONT'D. SITE 6. BUFFALO RIVER 600 YDS. DOWNSTREAM FROM SOUTH PARK BRIDGE. PAH SEDIMENT CONCENTRATIONS

	CONCENTRATIONS		
COMPOUND	WET ng/gm	DRY ng/gm	ORGANIC ng/mg
FLUORENE	320	630	20
PHENANTHRENE	1800	3600	100
ANTHRACENE	690	1400	42
FLUORANTHENE	1600	3200	100
MePHENANTHRENE	460	900	28
PYRENE	3600	7100	220
MeANTHRACENE	280	540	17
BENZOFLUORENE	3000	5900	180
BENZANTHRACENE	1300	2600	80
CHRYSENE	890	1800	54
BENZO(e)PYRENE	2100	4200	130
PERYLENE	4000	7900	240
BENZO(b)FLUORANTHENE	1000	2000	62
BENZO(k)FLUORANTHENE	580	1200	36
BENZO(a)PYRENE	1300	2500	79
DIBENZ(a,h)ANTHRACENE	230	450	14
BENZO(g,h,i)PERYLENE	1200	2400	73
INDENO(1,2,3-c,d)PYRENE	840	1700	51
TOTAL	2500	5000	1500

TABLE 1 CONT'D. SITE 7. BUFFALO RIVER 900 YDS. DOWNSTREAM FROM SOUTH PARK BRIDGE. PAH SEDIMENT CONCENTRATIONS

COMPOUND	CONCENTRATIONS WET ng/gm	 DRY ng/gm	 ORGANIC ng/mg
FLUORENE	120	240	6
PHENANTHRENE	1300	2500	61
ANTHRACENE	420	800	20
FLUORANTHENE	3400	6400	160
MePHENANTHRENE	540	1000	25
PYRENE	2800	5300	130
MeANTHRACENE	360	670	17
BENZOFLUORENE	3500	6600	160
BENZANTHRACENE	1200	2300	57
CHRYSENE	940	1800	44
BENZO(e)PYRENE	2100	3900	96
PERYLENE	3000	5600	140
BENZO(b)FLUORANTHENE	1300	2500	62
BENZO(k)FLUORANTHENE	590	1100	27
BENZO(a)PYRENE	1200	2200	55
DIBENZ(a,h)ANTHRACENE	270	500	12
BENZO(g,h,i)PERYLENE	1400	2600	64
INDENO(1,2,3-c,d)PYRENE	880	1700	41
TOTAL	25000	48000	1200

TABLE 1 CONT'D. SITE 8. BUFFALO RIVER IMMEDIATELY UPSTREAM FROM TURNING BASIN. PAH SEDIMENT CONCENTRATIONS

COMPOUND	CONCENTRATIONS WET ng/gm	 DRY ng/gm	 ORGANIC ng/mg
FLUORENE	76	130	4
PHENANTHRENE	820	1400	44
ANTHRACENE	400	700	22
FLUORANTHENE	2400	4100	130
MePHENANTHRENE	570	990	31
PYRENE	2100	3600	110
MeANTHRACENE	440	760	24
BENZOFLUORENE	3700	6400	200
BENZANTHRACENE	940	1600	51
CHRYSENE	740	1300	40
BENZO(e)PYRENE	2600	4500	140
PERYLENE	3700	6400	200
BENZO(b)FLUORANTHENE	930	1600	50
BENZO(k)FLUORANTHENE	370	640	20
BENZO(a)PYRENE	750	1300	40
DIBENZ(a,h)ANTHRACENE	160	270	9
BENZO(g,h,i)PERYLENE	780	1300	42
INDENO(1,2,3-c,d)PYRENE	160	2800	87
TOTAL	23000	40000	1200

TABLE 1 CONT'D. SITE 9. BUFFALO RIVER AT OHIO ST. BRIDGE. PAH SEDIMENT CONCENTRATIONS

COMPOUND	CONCENTRATIONS WET ng/gm	 DRY ng/gm	 ORGANIC ng/mg
FLUORENE	140	260	8
PHENANTHRENE	900	1700	51
ANTHRACENE	300	560	17
FLUORANTHENE	2400	4400	140
MePHENANTHRENE	300	560	17
PYRENE	1500	2700	84
MeANTHRACENE	220	400	12
BENZOFLUORENE	2200	4100	130
BENZANTHRACENE	560	100	32
CHRYSENE	350	650	20
BENZO(e)PYRENE	1900	3500	100
PERYLENE	2400	4500	140
BENZO(b)FLUORANTHENE	750	1400	42
BENZO(k)FLUORANTHENE	300	540	17
BENZO(a)PYRENE	560	1000	32
DIBENZ(a,h)ANTHRACENE	160	290	9
BENZO(g,h,i)PERYLENE	780	1400	44
INDENO(1,2,3-c,d)PYRENE	1100	2000	63
TOTAL	17000	31000	960

TABLE 1 CONT'D. SITE 10. BUFFALO RIVER AT NAVAL PARK PAH SEDIMENT CONCENTRATIONS

COMPOUND	CONCENTRATIONS WET ng/gm	DRY ng/gm	ORGANIC ng/mg
FLUORENE	86	170	5
PHENANTHRENE	880	1700	49
ANTHRACENE	300	600	17
FLUORANTHENE	2700	5300	150
MePHENANTHRENE	320	610	17
PYRENE	1800	3400	97
MeANTHRACENE	110	220	6
BENZOFLUORENE	2100	4000	110
BENZANTHRACENE	650	1200	36
CHRYSENE	360	700	20
BENZO(e)PYRENE	2000	4000	110
PERYLENE	2500	4900	140
BENZO(b)FLUORANTHENE	840	1600	47
BENZO(k)FLUORANTHENE	380	730	21
BENZO(a)PYRENE	670	1300	37
DIBENZ(a,h)ANTHRACENE	150	280	8
BENZO(g,h,i)PERYLENE	700	1400	39
INDENO(1,2,3-c,d)PYRENE	1100	2100	60
TOTAL	18000	34000	970

TABLE 2. LAKE ERIE: SITE 1. 300 YDS. OFFSHORE - 3 MILES SOUTH OF SMOKE CREEK MOUTH. PAH SEDIMENT CONCENTRATIONS

COMPOUND	CONCENTRATIONS WET ng/gm	 DRY ng/gm	 ORGANIC ng/mg
FLUORENE	39	48	3
PHENANTHRENE	280	340	21
ANTHRACENE	64	77	5
FLUORANTHENE	300	370	22
MePHENANTHRENE	45	55	3
PYRENE	190	230	14
MeANTHRACENE	25	30	2
BENZOFLUORENE	130	150	9
BENZANTHRACENE	89	110	7
CHRYSENE	72	87	5
BENZO(e)PYRENE	27	33	2
PERYLENE	130	160	10
BENZO(b)FLUORANTHENE	67	81	5
BENZO(k)FLUORANTHENE	43	52	3
BENZO(a)PYRENE	75	91	6
DIBENZ(a,h)ANTHRACENE	14	17	1
BENZO(g,h,i)PERYLENE	50	60	4
INDENO(1,2,3-c,d)PYRENE	51	62	4
TOTAL	1700	2100	130

TABLE 2 CONT'D. SITE 2. LAKE ERIE 300 YDS. OFFSHORE - 2 MILES SOUTH OF THE MOUTH OF SMOKE CREEK. PAH SEDIMENT CONCENTRATIONS

	CONCENTRATIONS		
COMPOUND	WET ng/gm	DRY ng/gm	ORGANIC ng/mg
FLUORENE	27	39	1
PHENANTHRENE	210	310	10
ANTHRACENE	38	55	2
FLUORANTHENE	440	640	21
MePHENANTHRENE	63	92	3
PYRENE	270	390	13
MeANTHRACENE	13	19	1
BENZOFLUORENE	89	130	4
BENZANTHRACENE	93	130	4
CHRYSENE	38	55	2
BENZO(e)PYRENE	45	64	2
PERYLENE	200	280	9
BENZO(b)FLUORANTHENE	74	110	3
BENZO(k)FLUORANTHENE	48	69	2
BENZO(a)PYRENE	75	110	4
DIBENZ(a,h)ANTHRACENE	14	21	1
BENZO(g,h,i)PERYLENE	54	79	3
INDENO(1,2,3-c,d)PYRENE	68	98	3
TOTAL	1900	2700	90

TABLE 2 CONT'D. SITE 3. LAKE ERIE 300 YDS. OFFSHORE - 2 MILES SOUTH OF THE MOUTH OF SMOKE CREEK. PAH SEDIMENT CONCENTRATIONS

COMPOUND	CONCENTRATIONS WET ng/gm	DRY ng/gm	ORGANIC ng/mg
FLUORENE	16	21	2
PHENANTHRENE	120	160	14
ANTHRACENE	15	20	2
FLUORANTHENE	270	350	30
MePHENANTHRENE	42	55	5
PYRENE	130	170	14
MeANTHRACENE	13	17	1
BENZOFLUORENE	78	100	9
BENZANTHRACENE	39	51	4
CHRYSENE	13	17	1
BENZO(e)PYRENE	25	33	3
PERYLENE	93	120	10
BENZO(b)FLUORANTHENE	38	50	4
BENZO(k)FLUORANTHENE	22	29	2
BENZO(a)PYRENE	32	42	4
DIBENZ(a,h)ANTHRACENE	7	9	1
BENZO(g,h,i)PERYLENE	29	38	3
INDENO(1,2,3-c,d)PYRENE	32	42	4
TOTAL	1000	1300	110

TABLE 2 CONT'D. SITE 4. LAKE ERIE 300 YDS. OFFSHORE - 3/4 MILES SOUTH OF MOUTH OF SMOKE CREEK. PAH SEDIMENT CONCENTRATIONS

COMPOUND	CONCENTRATIONS WET ng/gm	DRY ng/gm	ORGANIC ng/mg
FLUORENE	68	100	3
PHENANTHRENE	550	850	27
ANTHRACENE	91	140	4
FLUORANTHENE	920	1400	44
MePHENANTHRENE	120	190	5
PYRENE	460	710	22
MeANTHRACENE	35	53	2
BENZOFLUORENE	190	290	9
BENZANTHRACENE	190	290	9
CHRYSENE	ND*	ND	ND
BENZO(e)PYRENE	160	250	8
PERYLENE	300	460	14
BENZO(b)FLUORANTHENE	220	340	11
BENZO(k)FLUORANTHENE	110	160	5
BENZO(a)PYRENE	130	200	6
DIBENZ(a,h)ANTHRACENE	33	51	2
BENZO(g,h,i)PERYLENE	120	180	6
INDENO(1,2,3-c,d)PYRENE	140	220	7
TOTAL	3800	5900	180

*ND - Not Detected

TABLE 2 CONT'D. SITE 5. 300 YDS. OFFSHORE - WEST OF MOUTH OF SMOKE CREEK. PAH SEDIMENT CONCENTRATIONS

	CONCENTRATIONS		
COMPOUND	WET ng/gm	DRY ng/gm	ORGANIC ng/mg
FLUORENE	200	320	6
PHENANTHRENE	1500	2400	43
ANTHRACENE	330	530	10
FLUORANTHENE	1400	2200	41
MePHENANTHRENE	380	620	11
PYRENE	1400	2300	42
MeANTHRACENE	200	320	6
BENZOFLUORENE	1100	1800	34
BENZANTHRACENE	660	1100	19
CHRYSENE	630	1000	18
BENZO(e)PYRENE	410	660	12
PERYLENE	1600	2600	48
BENZO(b)FLUORANTHENE	600	970	18
BENZO(k)FLUORANTHENE	370	600	11
BENZO(a)PYRENE	740	1190	22
DIBENZ(a,h)ANTHRACENE	150	250	5
BENZO(g,h,i)PERYLENE	560	900	16
INDENO(1,2,3-c,d)PYRENE	610	980	18
TOTAL	13000	21000	380

TABLE 2 CONT'D. SITE 6. 300 YDS. OFFSHORE - 1/2 MILE NORTH OF MOUTH OF SMOKE CREEK

	CONCENTRATIONS		
COMPOUND	WET ng/gm	DRY ng/gm	ORGANIC ng/mg
FLUORENE	71	110	3
PHENANTHRENE	590	920	21
ANTHRACENE	89	140	3
FLUORANTHENE	1000	1600	37
MePHENANTHRENE	150	240	5
PYRENE	620	960	22
MeANTHRACENE	71	110	3
BENZOFLUORENE	200	310	7
BENZANTHRACENE	300	460	11
CHRYSENE	870	1400	31
BENZO(e)PYRENE	44	68	2
PERYLENE	360	560	13
BENZO(b)FLUORANTHENE	380	600	14
BENZO(k)FLUORANTHENE	170	270	6
BENZO(a)PYRENE	320	510	12
DIBENZ(a,h)ANTHRACENE	39	62	1
BENZO(g,h,i)PERYLENE	140	210	5
INDENO(1,2,3-c,d)PYRENE	180	280	7
TOTAL	5600	8800	200

TABLE 2 CONT'D. SITE 7. 300 YDS. OFFSHORE - 1 MILE NORTH OF MOUTH OF SMOKE CREEK. PAH SEDIMENT CONCENTRATIONS

	CONCENTRATIONS		
COMPOUND	WET ng/gm	DRY ng/gm	ORGANIC ng/mg
FLUORENE	150	200	10
PHENANTHRENE	990	1300	69
ANTHRACENE	310	420	22
FLUORANTHENE	1000	1400	71
MePHENANTHRENE	220	290	15
PYRENE	880	1200	61
MeANTHRACENE	180	240	13
BENZOFLUORENE	1100	1500	76
BENZANTHRACENE	280	380	20
CHRYSENE	200	270	14
BENZO(e)PYRENE	440	590	31
PERYLENE	420	560	29
BENZO(b)FLUORANTHENE	230	310	16
BENZO(k)FLUORANTHENE	130	180	9
BENZO(a)PYRENE	230	300	16
DIBENZ(a,h)ANTHRACENE	40	53	3
BENZO(g,h,i)PERYLENE	150	200	10
INDENO(1,2,3-c,d)PYRENE	180	240	12
TOTAL	7100	9600	500

TABLE 2 CONT'D. SITE 8. 1 1/2 MILES NORTH OF MOUTH OF SMOKE CREEK - 50 YDS. WEST OF POINT OF SOUTH HARBOR ENTRANCE BREAKWALL. PAH SEDIMENT CONCENTRATION

	CONCENTRATIONS		
COMPOUND	WET ng/gm	DRY ng/gm	ORGANIC ng/mg
FLUORENE	120	170	8
PHENANTHRENE	890	1300	56
ANTHRACENE	220	310	14
FLUORANTHENE	1500	2100	92
MePHENANTHRENE	210	300	13
PYRENE	830	1200	52
MeANTHRACENE	110	160	7
BENZOFLUORENE	820	1200	52
BENZANTHRACENE	550	780	35
CHRYSENE	440	630	28
BENZO(e)PYRENE	470	670	30
PERYLENE	1100	1600	72
BENZO(b)FLUORANTHENE	490	700	31
BENZO(k)FLUORANTHENE	320	460	20
BENZO(a)PYRENE	610	870	38
DIBENZ(a,h)ANTHRACENE	97	140	6
BENZO(g,h,i)PERYLENE	250	360	16
INDENO(1,2,3-c,d)PYRENE	410	590	26
TOTAL	9400	13500	596

TABLE 3. BETHLEHEM STEEL: SITE 1. 200 YDS. EAST OF ENTRANCE TO UNION CANAL. PAH SEDIMENT CONCENTRATIONS

	CONCENTRATIONS		
COMPOUND	WET ng/gm	DRY ng/gm	ORGANIC ng/mg
FLUORENE	2800	5600	37
PHENANTHRENE	12000	23000	160
ANTHRACENE	4300	8600	57
FLUORANTHENE	18000	36000	240
MePHENANTHRENE	2000	4000	27
PYRENE	11000	21000	140
MeANTHRACENE	1500	2900	19
BENZOFLUORENE	7800	15000	100
BENZANTHRACENE	3900	7700	51
CHRYSENE	2300	4600	31
BENZO(e)PYRENE	2500	5000	33
PERYLENE	7600	15000	99
BENZO(b)FLUORANTHENE	2300	4600	31
BENZO(k)FLUORANTHENE	1600	3100	21
BENZO(a)PYRENE	3200	6200	42
DIBENZ(a,h)ANTHRACENE	710	1400	9
BENZO(g,h,i)PERYLENE	1800	3500	23
INDENO(1,2,3-c,d)PYRENE	2600	5100	33
TOTAL	88000	172000	1200

TABLE 3 CONT'D. SITE 2. ENTRANCE TO UNION CANAL. PAH SEDIMENT CONCENTRATIONS

	CONCENTRATIONS		
COMPOUND	WET ng/gm	DRY ng/gm	ORGANIC ng/mg
FLUORENE	1500	2700	20
PHENANTHRENE	7100	13000	96
ANTHRACENE	3000	5500	40
FLUORANTHENE	13000	23000	170
MePHENANTHRENE	1400	2500	19
PYRENE	6800	1300	92
MeANTHRACENE	960	1800	13
BENZOFLUORENE	5100	9400	69
BENZANTHRACENE	2900	5400	39
CHRYSENE	2300	4300	32
BENZO(e)PYRENE	2800	5200	38
PERYLENE	7900	15000	110
BENZO(b)FLUORANTHENE	1900	3500	26
BENZO(k)FLUORANTHENE	1300	2400	18
BENZO(a)PYRENE	2300	4300	32
DIBENZ(a,h)ANTHRACENE	530	990	7
BENZO(g,h,i)PERYLENE	1400	2500	19
INDENO(1,2,3-c,d)PYRENE	1600	3100	22
TOTAL	64000	110000	860

TABLE 3 CONT'D. SITE 3. ENTRANCE TO LACKAWANNA CANAL. PAH SEDIMENT CONCENTRATIONS

	CONCENTRATIONS		
COMPOUND	WET ng/gm	DRY ng/gm	ORGANIC ng/mg
FLUORENE	1300	1900	26
PHENANTHRENE	5800	8600	120
ANTHRACENE	2200	3200	45
FLUORANTHENE	9400	14000	190
MePHENANTHRENE	930	1400	19
PYRENE	9200	14000	190
MeANTHRACENE	710	1100	15
BENZOFLUORENE	2800	4200	58
BENZANTHRACENE	3100	4500	63
CHRYSENE	3500	5200	72
BENZO(e)PYRENE	1900	2700	38
PERYLENE	3300	4900	69
BENZO(b)FLUORANTHENE	1800	2700	38
BENZO(k)FLUORANTHENE	1100	1600	23
BENZO(a)PYRENE	2700	40000	56
DIBENZ(a,h)ANTHRACENE	450	670	1
BENZO(g,h,i)PERYLENE	2100	3000	42
INDENO(1,2,3-c,d)PYRENE	1300	1900	26
TOTAL	54000	80000	1100

TABLE 3 CONT'D. SITE 4. 1/8 MILE NORTH OF ENTRANCE TO LACKAWANNA CANAL.
PAH SEDIENT CONCENTRATIONS

	CONCENTRATIONS		
COMPOUND	WET ng/gm	DRY ng/gm	ORGANIC ng/mg
FLUORENE	240	400	5
PHENANTHRENE	1800	2900	34
ANTHRACENE	560	940	11
FLUORANTHENE	3400	5600	64
MePHENANTHRENE	320	530	6
PYRENE	2100	3500	40
MeANTHRACENE	180	290	3
BENZOFLUORENE	980	1600	19
BENZANTHRACENE	960	1600	18
CHRYSENE	650	1100	12
BENZO(e)PYRENE	750	1200	14
PERYLENE	1400	2400	27
BENZO(b)FLUORANTHENE	730	1200	14
BENZO(k)FLUORANTHENE	500	820	9
BENZO(a)PYRENE	850	1400	16
DIBENZ(a,h)ANTHRACENE	170	290	3
BENZO(g,h,i)PERYLENE	590	980	11
INDENO(1,2,3-c,d)PYRENE	770	1300	15
TOTAL	17000	28000	320

TABLE 3 CONT'D. SITE 5. 1/4 MILE NORTH OF ENTRANCE TO LACKAWANNA CANAL. PAH SEDIMENT CONCENTRATIONS

COMPOUND	CONCENTRATIONS WET ng/gm	DRY ng/gm	ORGANIC ng/mg
FLUORENE	270	570	5
PHENANTHRENE	1800	3900	32
ANTHRACENE	520	1100	9
FLUORANTHENE	3400	7200	59
MePHENANTHRENE	530	1100	9
PYRENE	2100	4400	36
MeANTHRACENE	2300	480	4
BENZOFLUORENE	1400	3000	25
BENZANTHRACENE	920	2000	16
CHRYSENE	720	1500	13
BENZO(e)PYRENE	150	320	3
PERYLENE	1700	3600	29
BENZO(b)FLUORANTHENE	680	1500	12
BENZO(k)FLUORANTHENE	490	1000	9
BENZO(a)PYRENE	840	1800	15
DIBENZ(a,h)ANTHRACENE	160	350	3
BENZO(g,h,i)PERYLENE	500	1100	9
INDENO(1,2,3-c,d)PYRENE	730	1600	13
TOTAL	17000	37000	300

TABLE 3 CONT'D. SITE 6: 3/8 MILE NORTH OF ENTRANCE TO LACKAWANNA CANAL.
PAH SEDIMENT CONCENTRATIONS

COMPOUND	CONCENTRATIONS WET ng/gm	DRY ng/gm	ORGANIC ng/mg
FLUORENE	150	270	3
PHENANTHRENE	1300	2300	26
ANTHRACENE	340	610	7
FLUORANTHENE	2500	4500	51
MePHENANTHRENE	250	450	5
PYRENE	1400	2500	29
MeANTHRACENE	150	260	3
BENZOFLUORENE	980	1800	20
BENZANTHRACENE	720	1300	15
CHRYSENE	540	990	11
BENZO(e)PYRENE	600	1100	12
PERYLENE	1200	2100	24
BENZO(b)FLUORANTHENE	590	1100	12
BENZO(k)FLUORANTHENE	390	700	8
BENZO(a)PYRENE	670	1200	14
DIBENZ(a,h)ANTHRACENE	140	250	3
BENZO(g,h,i)PERYLENE	520	940	11
INDENO(1,2,3-c,d)PYRENE	600	1100	13
TOTAL	13000	23000	270

TABLE 4. TWO MILE CREEK: SITE 1. AT RIVER ROAD BRIDGE. PAH SEDIMENT CONCENTRATIONS

COMPOUND	CONCENTRATIONS		
	WET ng/gm	DRY ng/gm	ORGANIC ng/mg
FLUORENE	ND	ND	ND
PHENANTHRENE	290	540	5
ANTHRACENE	ND	ND	ND
FLUORANTHENE	3500	6500	66
MePHENANTHRENE	90	170	2
PYRENE	590	1100	11
MeANTHRACENE	92	170	2
BENZOFLUORENE	1700	3100	81
BENZANTHRACENE	2600	4900	49
CHRYSENE	2800	5100	51
BENZO(e)PYRENE	2800	5100	51
PERYLENE	6600	12000	120
BENZO(b)FLUORANTHENE	3300	6000	61
BENZO(k)FLUORANTHENE	1600	3000	30
BENZO(a)PYRENE	3300	6000	61
DIBENZ(a,h)ANTHRACENE	1600	3000	30
BENZO(g,h,i)PERYLENE	2800	5200	52
INDENO(1,2,3-c,d)PYRENE	3000	5600	56
TOTAL	37000	6700	730

ND - Not Detected

TABLE 4 CONT'D. SITE 2. INTERMITTENT TRIBUTARY TO TWO MILE CREEK 1/4 MILE SOUTHWEST OF TWO MILE CREEK ROAD. PAH SEDIMENT CONCENTRATIONS

COMPOUND	CONCENTRATIONS		
	WET ng/gm	DRY ng/gm	ORGANIC ng/mg
FLUORENE	190	350	2
PHENANTHRENE	1300	2400	17
ANTHRACENE	330	630	4
FLUORANTHENE	3600	6900	47
MePHENANTHRENE	1400	2700	18
PYRENE	ND*	ND	ND
MeANTHRACENE	570	1100	7
BENZOFLUORENE	570	1100	7
BENZANTHRACENE	360	700	5
CHRYSENE	690	1300	9
BENZO(e)PYRENE	480	910	6
PERYLENE	980	1900	13
BENZO(b)FLUORANTHENE	310	590	4
BENZO(k)FLUORANTHENE	160	300	2
BENZO(a)PYRENE	300	590	4
DIBENZ(a,h)ANTHRACENE	80	150	1
BENZO(g,h,i)PERYLENE	410	790	5
INDENO(1,2,3-c,d)PYRENE	220	430	3
TOTAL	12000	23000	150

ND - Not Detected

TABLE 4 CONT'D. SITE 3. INTERMITTENT TRIBUTARY TO TWO MILE CREEK 1/2 MILE SOUTHWEST OF TWO MILE CREEK ROAD. PAH SEDIMENT CONCENTRATIONS

	CONCENTRATIONS		
COMPOUND	WET ng/gm	DRY ng/gm	ORGANIC ng/mg
FLUORENE	1100	2200	13
PHENANTHRENE	5300	11000	65
ANTHRACENE	1400	2800	17
FLUORANTHENE	2100	43000	260
MePHENANTHRENE	2800	5700	34
PYRENE	62000	130000	770
MeANTHRACENE	3700	7400	45
BENZOFLUORENE	16000	33000	200
BENZANTHRACENE	1700	3500	21
CHRYSENE	43	88	1
BENZO(e)PYRENE	3700	7600	46
PERYLENE	ND*	ND	ND
BENZO(b)FLUORANTHENE	540	1100	7
BENZO(k)FLUORANTHENE	210	440	3
BENZO(a)PYRENE	290	580	4
DIBENZ(a,h)ANTHRACENE	99	200	1
BENZO(g,h,i)PERYLENE	420	850	5
INDENO(1,2,3-c,d)PYRENE	350	710	4
TOTAL	120000	250000	1500

*ND - Not Detected

TABLE 5. MOUTH OF FRENCHMAN'S CREEK, CANADA. PAH SEDIMENT CONCENTRATIONS

COMPOUND	CONCENTRATIONS WET ng/gm	DRY ng/gm	ORGANIC ng/mg
FLUORENE	9	13	0.7
PHENANTHRENE	110	150	7.1
ANTHRACENE	7	11	0.5
FLUORANTHENE	320	430	21
MePHENANTHRENE	34	47	2.3
PYRENE	190	250	12
MeANTHRACENE	11	16	0.8
BENZOFLUORENE	66	90	4.4
BENZANTHRACENE	36	50	2.5
CHRYSENE	ND*	ND	ND
BENZO(e)PYRENE	ND	ND	ND
PERYLENE	43	60	2.9
BENZO(b)FLUORANTHENE	130	180	8.8
BENZO(k)FLUORANTHENE	26	36	1.7
BENZO(a)PYRENE	46	63	3.1
DIBENZ(a,h)ANTHRACENE	8	11	0.5
BENZO(g,h,i)PERYLENE	31	44	2.1
INDENO(1,2,3-c,d)PYRENE	43	59	2.9
TOTAL	1100	1500	74

*ND - Not Detected

TABLE 6. MOUTH OF BLACK CREEK, CANADA. PAH SEDIMENT CONCENTRATIONS

COMPOUND	CONCENTRATIONS WET ng/gm	DRY ng/gm	ORGANIC ng/mg
FLUORENE	14	21	0.5
PHENANTHRENE	40	60	1.4
ANTHRACENE	19	30	0.7
FLUORANTHENE	120	180	4.1
MePHENANTHRENE	20	29	0.7
PYRENE	7	11	0.3
MeANTHRACENE	6	9	0.2
BENZOFLUORENE	40	60	1.4
BENZANTHRACENE	11	16	0.4
CHRYSENE	ND*	ND	0.4
BENZO(e)PYRENE	ND	ND	ND
PERYLENE	12	17	ND
BENZO(b)FLUORANTHENE	7.3	11	0.4
BENZO(k)FLUORANTHENE	3.1	4.6	0.3
BENZO(a)PYRENE	11.0	17	0.1
DIBENZ(a,h)ANTHRACENE	4.0	6	0.4
BENZO(g,h,i)PERYLENE	11.0	17	0.1
INDENO(1,2,3-c,d)PYRENE	ND	ND	0.4
			ND
TOTAL	330	490	11

*ND - Not Detected

TABLE 7. TONAWANDA CREEK 1/4 MILE FROM CONFLUENCE WITH NIAGARA RIVER PAH SEDIMENT CONCENTRATIONS

	CONCENTRATIONS		
COMPOUND	WET ng/gm	DRY ng/gm	ORGANIC ng/mg
FLUORENE	57	140	3
PHENANTHRENE	1400	3400	67
ANTHRACENE	260	640	12
FLUORANTHENE	4500	11000	210
MePHENANTHRENE	280	700	14
PYRENE	2700	6700	130
MeANTHRACENE	150	360	7
BENZOFLUORENE	1000	2500	49
BENZANTHRACENE	920	2300	44
CHRYSENE	980	2400	47
BENZO(e)PYRENE	720	1800	34
PERYLENE	2600	6300	120
BENZO(b)FLUORANTHENE	1500	3700	73
BENZO(k)FLUORANTHENE	680	1700	32
BENZO(a)PYRENE	1000	2500	49
DIBENZ(a,h)ANTHRACENE	160	390	8
BENZO(g,h,i)PERYLENE	840	2100	40
INDENO(1,2,3-c,d)PYRENE	890	2200	42
TOTAL	21000	5100	1000

APPENDIX C

Appendix C

Site Descriptions of Sampling Sites in Text
(Site Descriptions for Figures Not Listed in Appendix Are Included in Text)

Figure 1

Site 1.	Smoke Creek
Site 2.	Union Canal
Site 3.	Lackawanna Canal (mouth)
Site 4.	Lackawanna Canal
Site 5.	Small Boat Harbor A
Site 6.	Small Boat Harbor B
Site 7.	Buffalo River A (breakwall)
Site 8.	Buffalo River B (Naval Park)
Site 9.	Allied Chemical (downstream, left bank)
Site 10.	Allied Chemical (downstream, right bank)
Site 11.	Republic Steel
Site 12.	Buffalo Color
Site 13.	Scajaquada A
Site 14.	Scajaquada B
Site 15.	Buffalo Sewer Authority
Site 16.	Sheridan Drive
Site 17.	Niagara Mohawk
Site 18.	Two Mile Creek A
Site 19.	Two Mile Creek B
Site 20.	Tonawanda Creek A
Site 21.	Tonawanda Creek B
Site 22.	Frenchman's Creek A
Site 23.	Frenchman's Creek B
Site 24.	Black Creek A
Site 25.	Black Creek B

Figure 2

Site 1.	Buffalo River downstream from confluence of N. and S. branches
Site 2.	Buffalo River at downstream boundary of Mobil Tank Farm
Site 3.	Buffalo River 200 yds. upstream of South Park Bridge
Site 4.	Buffalo River at South Park Bridge
Site 5.	Buffalo River at Buffalo Color
Site 6.	Buffalo River 600 yds. downstream from South Park Bridge
Site 7.	Buffalo River 900 yds. downstream from South Park Bridge
Site 8.	Buffalo River immediately upstream from turning basin
Site 9.	Buffalo River at Ohio Street Bridge
Site 10.	Buffalo River at Naval Park

Figure 3

Site 1.	300 yds. off shore - 3 miles south of the mouth of Smokes Creek
Site 2.	300 yds. off shore - 2 miles south of the mouth of Smokes Creek
Site 3.	300 yds. off shore - 1.5 miles south of the mouth of Smokes Creek
Site 4.	300 yds. off shore - 3/4 miles south of Smokes Creek
Site 5.	300 yds. off shore - west of mouth of Smokes Creek
Site 6.	300 yds. off shore - 1/2 mile north of mouth of Smokes Creek
Site 7.	300 yds. off shore - 1 mile north of mouth of Smokes Creek
Site 8.	1 1/2 miles north of mouth of Smokes Creek - mouth 50 yds west of point of South Harbor entrance breakwall

Figure 4

Site 1.	200 yds. east of entrance to Union Canal
Site 2.	Entrance to Union Canal
Site 3.	Entrance to Lackawanna Canal
Site 4.	1/8 mile north of entrance to Lackawanna Canal
Site 5.	1/4 mile north of entrance to Lackawanna Canal
Site 6.	3/8 mile north of entrance to Lackawanna Canal

Figure 5

Site 1.	Two Mile Creek at River Road Bridge
Site 2.	Intermittent Tributary to Two Mile Creek 1/4 Mile Southwest of Two Mile Creek Road
Site 3.	Intermittent Tributary to Two Mile Creek 1/2 Mile Southwest of Two Mile Creek Road

Figure 6

Site 1.	Mouth of Black Creek
Site 2.	Mouth of Frenchmans Creek
Site 3.	Mouth of Tonawanda Creek
Site 4.	Buffalo River at South Park Bridge
Site 5.	Buffalo River at Naval Park
Site 6.	Buffalo River at Republic Steel
Site 7.	Buffalo River at Buffalo Color
Site 8.	Lackawanna Canal
Site 9.	Union Canal
Site 10.	Two Mile Creek

Figure 7

Site 1. Second bridge This artificial substrate was anchored on the downstream side of the second bridge on the left (easterly) fork of the river.

Site 2. Second bridge This artificial substrate was anchored below the second bridge on the right (westerly) branch of the river. It was near the right bank (facing upstream) just below what appears to be a storm sewer drain.

Site 3. Allied Chemical This artificial substrate was located immediately below the effluents at Allied Chemical.

Site 4. South Park bridge This artificial substrate was approximately 20 yards below the South Park Avenue bridge along the Buffalo Color plant wall (right bank) approximately 3 to 6 feet from the shore.

Site 5. South Park bridge This artificial substrate was on the opposite bank across from site 4.

Site 6. Buffalo Color This artificial substrate was anchored 5 to 10 yards below the effluent baffle about 6 to 10 feet from the left bank.

Site 7. Republic Steel effluent This artificial substrate was "swimming" directly in the effluent turbulence of the first major effluent encountered downstream of the South Park bridge. This is approximately 150 yards below the old Railroad bridge.

Site 8. River bend This artificial substrate was located along the left bank (east side) at the bend below Buffalo Color.

Site 9. Republic Steel This artificial substrate was located about 20 yards below the second Republic Steel effluent almost directly opposite site 11.

Site 10. R.R. bridge This artificial substrate was in midstream just above the old railroad bridge.

Site 11. Second R.R. bridge This artificial substrate was just upstream of the R.R. bridge approximately 1 mile from the site 13 bridge. It was located slightly to the west of the main part of the channel.

Figure 10

Site 1.	Lake Erie This artificial substrate was just on the south edge of the current from Smoke Creek flowing into Lake Erie approximately 75 yards from shore.
Site 2.	Lake Erie This artificial substrate was on the north edge of the Smoke Creek current where it flows into Lake Erie approximately 75 yards offshore.
Site 3.	Sewer overflow This artificial substrate was located less than 10 feet from the sewer opening at Roland and Front Streets in Lackawanna in the edge of the heavy flows created when the station operates.
Site 4.	Seal Place bridge This artificial substrate was anchored 75 to 100 yards upstream of the bridge at Warsaw Street in Lackawanna near the shore property of Mr. Ed Buczek.
Site 5.	Pedestrian bridge This artificial substrate was anchored about 50 feet downstream below a metal pedestrian bridge located at a gravel road that runs behind the Buffalo Railroad shop off Dona Street in Lackawanna. The artificial substrate was near the north shore.
Site 6.	Route 5 bridge This artificial substrate was located approximately 6 feet from shore just upstream of the bridge.
Site 1UL	Union Lackawanna 1 This artificial substrate was placed approximately 10 yards from the north side of the canal, directly opposite an effluent boom that is 40 to 50 yards inside the canal.
2UL	Union Lackawanna 2 There is an effluent grating located just around the corner from the Union Chip Canal (southerly direction). The artificial substrate was anchored within 6 feet of the wall and about 25 yards from the grating.

Figure 11

B R 1-10 - Buffalo River
S M 1-8 - Lake Erie Transect across the mouth of Smokes Creek
U L 1-6 - Union and Lackawanna Canals
T M 1-3 - Two Mile Creek 1-3
B L 1 - Black Creek mouth
F R 1 - Niagara River
F R 1 - Frenchman's Creek mouth at Niagara River
Ton - Tonawanda Creek mouth at Niagara River

Figure 12

Site 1. River Road bridge This artificial substrate was anchored at the mouth of Two Mile Creek near the River Road bridge.

Site 2. Two Mile Road conduit This artificial substrate was located 30 feet below the effluent pipe and a minor (intermittent) tributary near Two Mile Road.

Site 3. Veterans Park This artificial substrate was anchored near a storage facility above major and minor flows.

APPENDIX D

QUALITY CONTROL MEASURES

1. Solvents: Hydrocarbon solvents were redistilled from technical grade solvents producing a high quality solvent at low cost. The quality of the redistilled product from each new 5 gallon batch of solvent was checked out by evaporating 30 mls of hydrocarbon solvent into a 100ul volume of DMSO in a conical centrifuge tube. A 10ul aliquot was injected into the HPCL and the elution monitored at 0.016 AUF, 254 nM UV absorbance. This technique provides more than a 600-fold comparative solvent concentration factor since most real samples were analyzed at sensitivities of 0.04 AUF to 0.08 AUF, 254 nM. Typical chromatograms demonstrating the improvement in solvent quality are shown in figures QC 1. and QC 2. Solvent quality produced by the distillation appeared to be very uniform within each solvent type regardless of the source or degree of pre-distillation contamination. Differences in quality between commercially redistilled solvents and those prepared using the Fisher refluxing condenser were negligible relative to contamination as visualized by HPLC/UV detection.

2. Peak resolution: Environmental samples contain certain complex mixtures of biogenic and anthropogenic chemicals which are difficult to separate by any chromatographic methods, the combinations of alcoholic hydrolysis, solvent partitioning, and Florisil chromatography generally produced fractions which exhibited a characteristic peak distribution. Although many peaks were only partly resolved from neighboring components, use of "in series"

detection by absorbance at 254 nM followed by monochromatic fluorescence detection (EX 295, EM 405) reduced the degree of uncertainty associated with measurement of some PAH. Typical chromatograms illustrating the character of the peak resolution in analysis of sediment fractions are shown in Figure QC 3. This figure shows absorbance chromatograms of sediment collected from the Buffalo Harbor (sediment sample taken at the intersection of a line from the Lackawanna Bethlehem Steel and Union ship canals near the Bethlehem Steel Corporation) together with a companion chromatogram of a spiked sample. Figure QC 4. shows the companion fluorescence chromatograms produced by analysis of these same two fractions (spiked and non-spiked).

3. Blanks: Although reagent blanks were not run for every new batch of solvents (quality checked by the previously described procedure), periodic reagent blanks using the technical grade redistilled solvents exhibited very few artificial peaks (Figure QC 5.). At the sensitivities and sample concentrations used in the present project, trace amounts of phenanthrene (not exceeding 5.0 ng), benzo(k)fluoranthene, and benzo(a)pyrene (not exceeding 0.5 ng) could be found (see tabular data for typical blank results).

4. Replicates: Replicates of three injections each, were run on two sediment samples (S-16-82) and (S-16-82 dup.). Standard deviation for each PAH varied within and between samples but most were less than 10% of the individual PAH concentration (see tabular values).

5. Duplicates: Three sediment samples were run as paired duplicates. Although individual PAH values varied in the range of 10% between samples, overall there was a reasonable agreement between pairs of duplicates (see tabular values for results of analysis of paired duplicates).

6. Recovery rates: Recovery rates were calculated for two spiked sediment samples (also run as duplicates). Recovery rates for one sample averaged 90 - 100% (S-16-82) and 75 - 85% for the other sample S-29-82 (see tabular values). Recovery rates were measured for a water sample processed using a commercial C_{18} reversed phase mini-column chromatography cartridge (J.T. Baker; 6ml capacity). Recoveries of PAH compounds from these cartridges were in the low range, i.e. 25 - 40% indicating the cartridge trapping technique will significantly underestimate (by as much as 60 - 80%) the concentrations/amounts of PAH in aqueous effluent. In this regard, PAH values for effluent 225 should be compared as this effluent was analyzed both by the cartridge trapping technique and by conventional liquid extraction (dichloromethane extraction).

7. Polypropylene substrates: Polypropylene substrates were used as an integrative indexing procedure for comparing relative amounts of PAH adsorbed from water over a measured length of time. The technique does not yield quantitative information in terms of effluent concentrations, but aspects of the efficiency with which PAH can be recovered from the substrates, as well as the reproducibility of the technique, have been studied (see Black, Hart, and Black (1982). Environ. Sci. Technol. 16: 247-250).

8. Cleaning and Preparation of ISCO Sampling Devices:

Sampler tubing is cleaned as follows:

a) Wash with non-phosphate detergent in hot water

8. Cleaning and Preparation of ISCO Sampling Devices (continued)

b) Rinse with hot water

c) Remove stainless steel sampling probe from sampling tube

d) One liter of HCl (one part distilled water; one part concentrated HCl) is run through tubing

e) A rinse with hot tap water follows (12L)

f) Two liters of distilled water are run through tubing

Prior to collection of sample:

a) ISCO sampler is flushed continuously with water to be sampled

b) Wastewater is collected in glass bottles

Grab Water Samples:

a) Stainless steel buckets are used (cleaning methods follow)

b) Prior to taking sample, bucket is rinsed 3 times with sample water source

c) Water samples are taken with glass vials without any visible air remaining in container

d) A cleaned bucket is used for each sample taken, and clean buckets are used each day for grab samples

Sediment Samples:

a) Ponar or Eckman dredges are rinsed repeatedly in water at each sediment sampling site. After a sediment sample is obtained the dredges are scraped of visible residue and repeatedly rinsed in water again.

Cleaning of Sampling Containers for Water Samples:

a) Scrub with steel wool and acetone

b) Rinse with hot water

c) Wash with hot soapy water

d) Rinse with hot water

e) Rinse with distilled water

f) Acetone rinse with reagent grade acetone

Cleaning of Sampling Containers for Water Samples (continued)

g) Rinse with 100 ml of reagent grade ether

h) Rinse aluminum foil with petroleum grade ether and cover buckets

Plastic bottles:

a) All plastic bottles are soap washed

b) Tap water rinsed

c) Nitric acid washed

d) Rinsed a minimum of 4 times with deionized water

All glass bottles are:

a) Soap washed

b) Tap water rinsed

c) Rinsed with pesticide grade ether

d) Rinsed a minimum of six times with deionized water

FIGURE QC 1.

TECHNICAL GRADE HEXANE

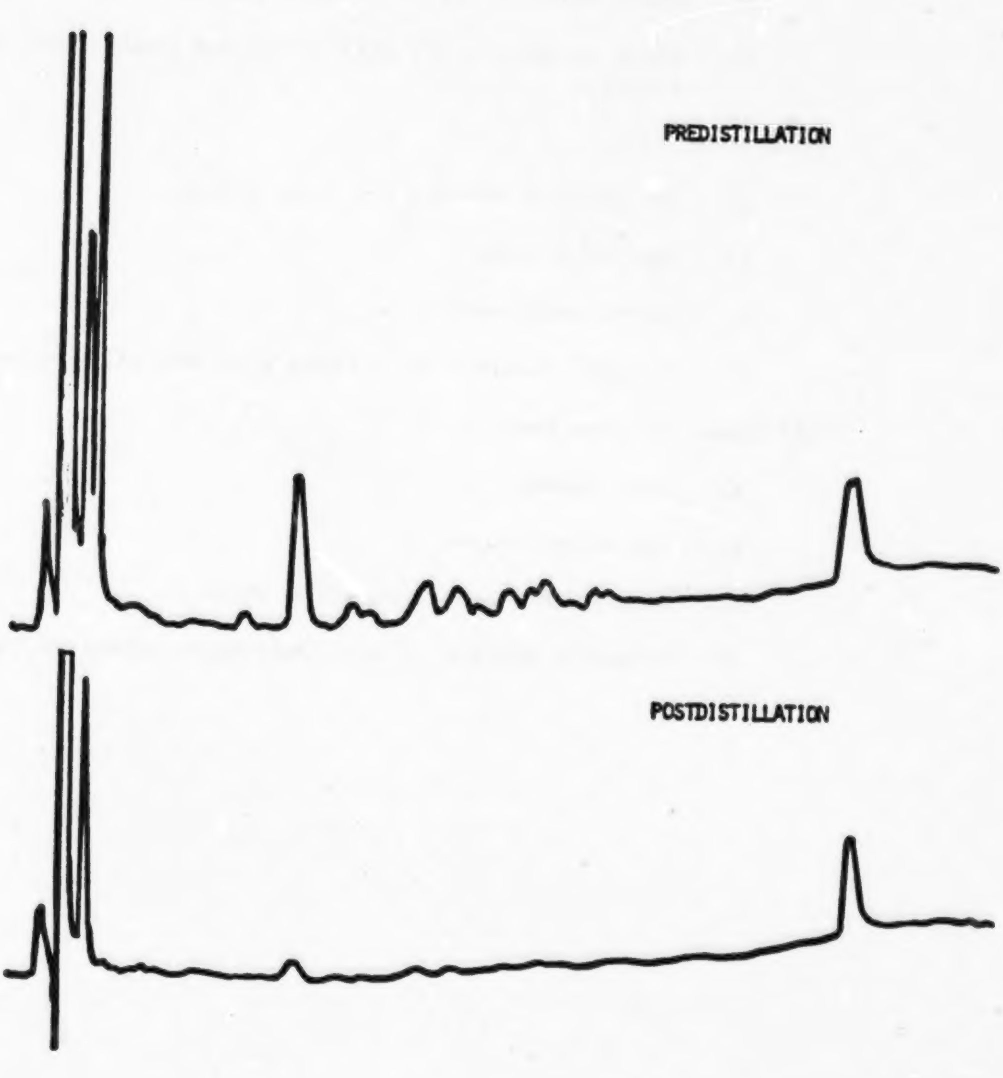


FIGURE QC 2.

TECHNICAL GRADE ISO-OCTANE

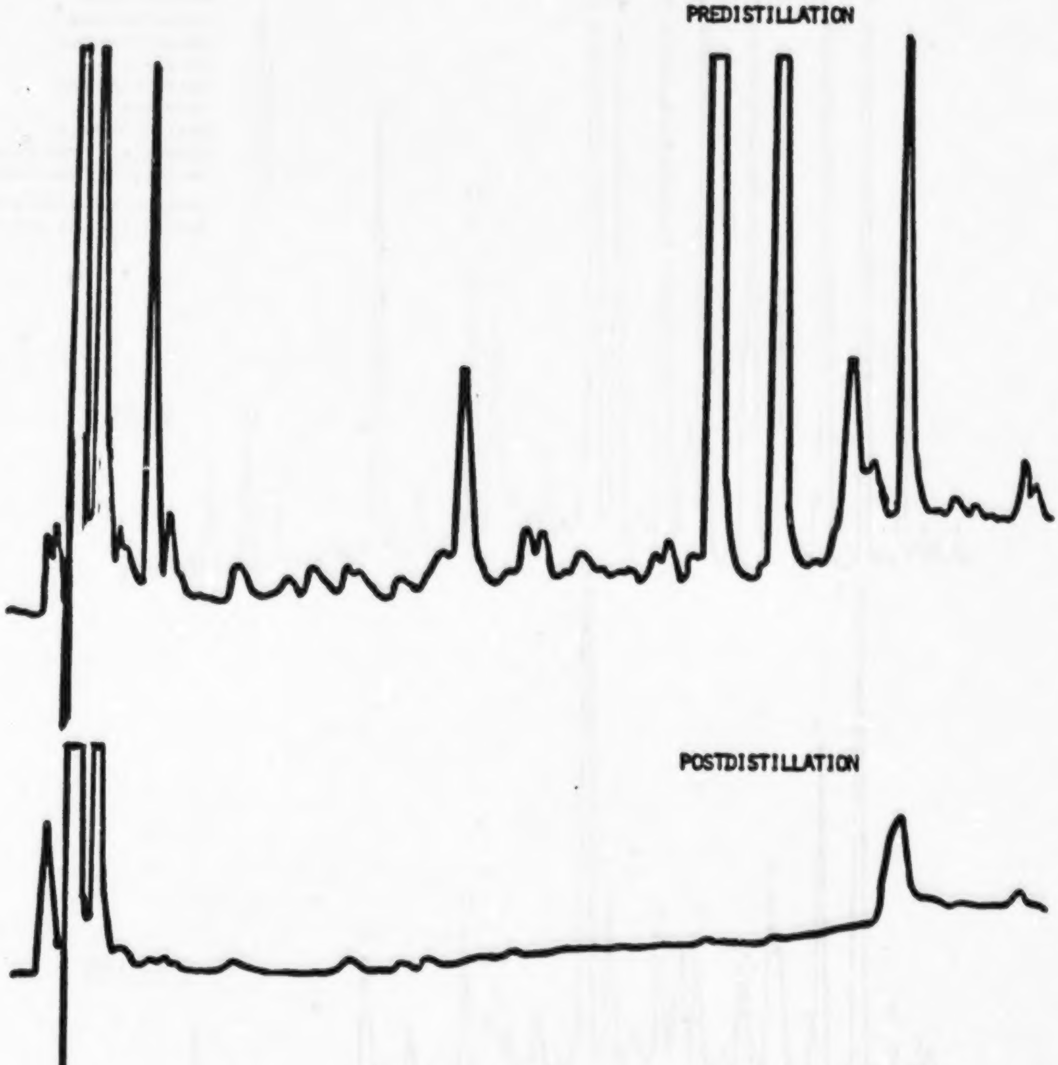


FIGURE QC 3.

ABSORBANCE CHROMATOGRAM

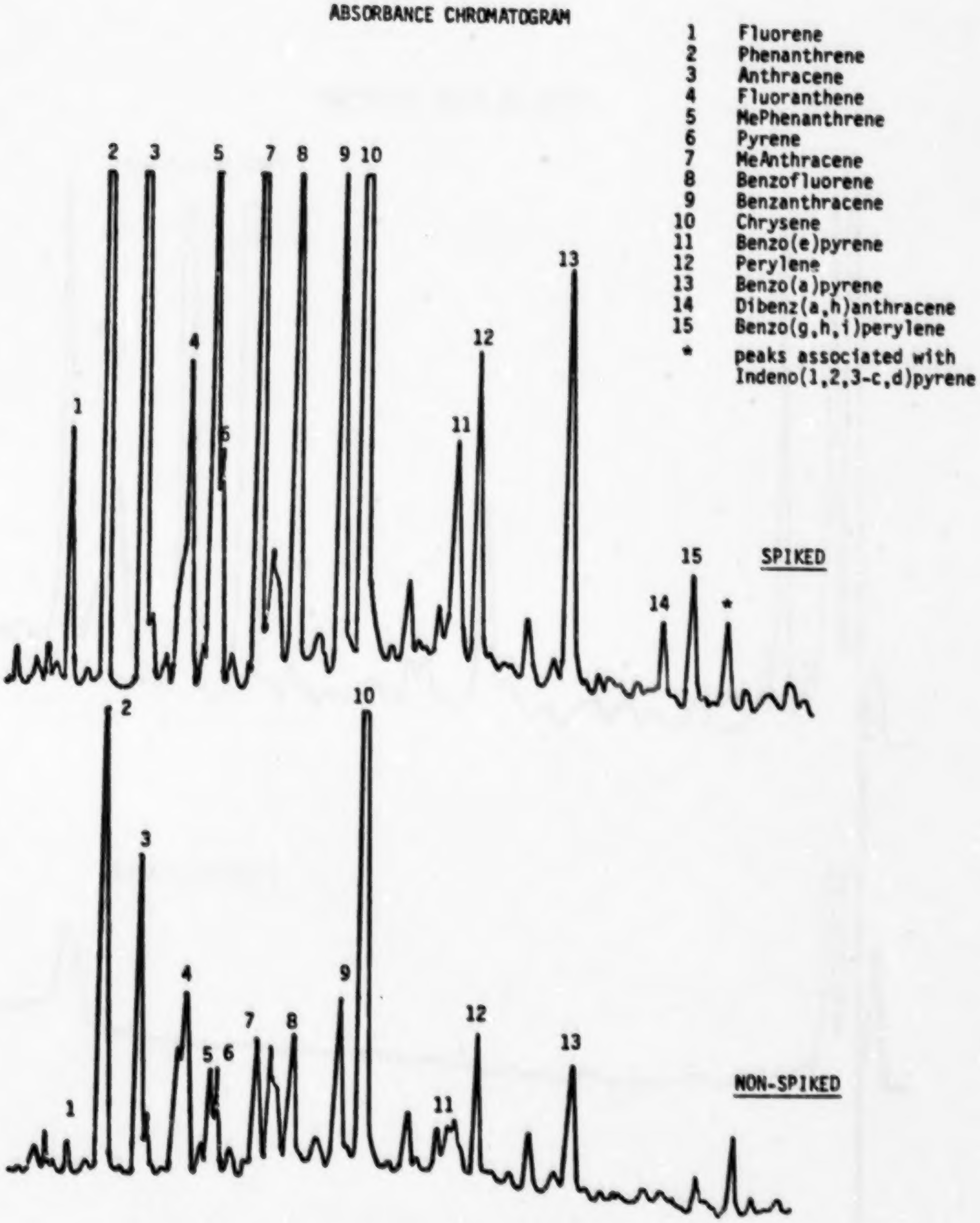


FIGURE QC 4.

FLUORESCENCE CHROMATOGRAM

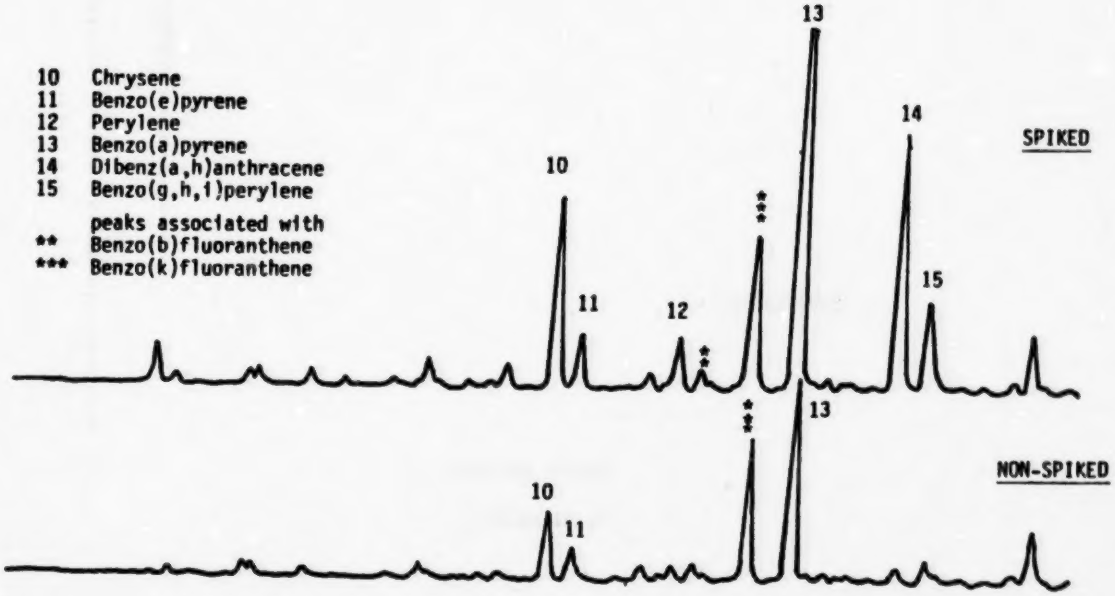
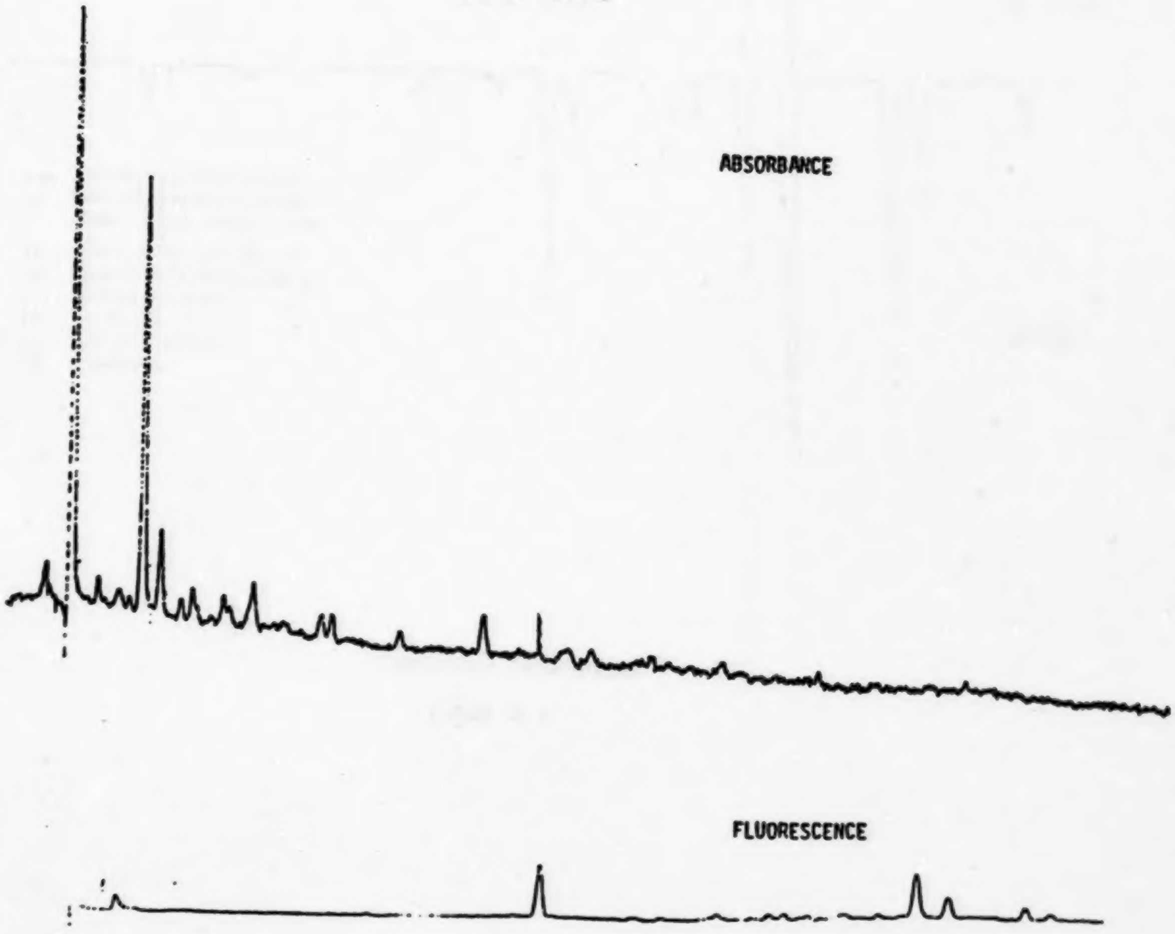


FIGURE QC 5.

REAGENT BLANKS



PAH CONCENTRATIONS FOR AQUEOUS EFFLUENT 225 (ng/liter)

Liquid Ex. Dichloromethane C_{18}

Sample name		Effluent 225		Effluent 225				
Sample vol (ul)		340		500				
Sample inject (ul)		5		1.5				
Wet wt (gm)		3420		1679				
Dry wt (mg)								
Organic wt (mg)								
No. of compounds		18		18				
1 Fluorene		873.200		0				
2 Phenanthrene		16,829.600		0				
3 Anthracene		957.200		0				
4 Fluoranthene		71,095.600		56,298.004				
5 MePhenanth		6,098.800		0				
6 Pyrene		13,989.600		15,522.355				
7 MeAnthracene		834.200		0				
8 Benzofluor		12,230.200		0				
9 Benzanth		3,712.400		2,979.840				
10 Chrysene		4,202.200		7,534.930				
Benzo(e)pyr		10,635.200		0				
12 Perylene		12,085.800		0				
13 Benzo(b)fluor		4,510.000		1,956.487				
14 Benzo(k)fluor		1,471.400		972.455				
15 Benzo(a)pyr		1,498.200		973.054				
16 Dibenz(a,h)anth		404.200		97.206				
17 Benzo(g,h,i)peryl		2,704.400		1,500.00				
18 Indeno(1,2,3-c,d)pyr		------		0				

REAGENT BLANK
ng/gm

VARIATION WITHIN SAMPLES
ng/gm

Sample name	Blank		S-16-82			S-16-82 duplicate		
Sample vol (ul)	1000		1000			1000		
Sample inject (ul)	10		2.5			2.5		
Wet wt (gm)			5.0			5.0		
Dry wt (mg)								
Organic wt (mg)								
No. of compounds	18		18	St. dev.*			St. dev.*	
1 Fluorene	0		249	29.7		255	32.5	
2 Phenanthrene	4.8		1781	8.62		1775	47.0	
3 Anthracene	0		598	10.5		531	12.4	
4 Fluoranthene	0		3499	88.1		3214	45.8	
5 MePhenanth	0		323	10.5		318	39.7	
6 Pyrene	0		2216	267.0		2048	552.0	
7 MeAnthracene	0		161	25.3		194	11.5	
8 Benzofluor	0		913	17.4		1043	14.0	
9 Benzanth	0		994	54.8		916	72.8	
10 Chrysene	0		684	79.2		609	35.2	
11 Benzo(e)pyr	0		683	49.5		642	22.9	
12 Perylene	0		1483	11.2		1377	67.1	
13 Benzo(b)fluor	0		759	15.1		697	21.0	
14 Benzo(k)fluor	0.33		483	12.0		467	37.5	
15 Benzo(a)pyr	0.42		872	48.2		815	42.6	
16 Dibenz(a,h)anth	0		161	11.0		159	3.5	
17 Benzo(g,h,i)peryl	0		587	46.2		566	34.0	
18 Indeno(1,2,3-c,d)pyr	0		734	26.8		805	14.6	

* Based on 3 replicate injections of each sample

SEDIMENT DUPLICATES (ng/gm)

Sample name	S-8-82	S-8-82 dup.		S-16-82	S-16-82 dup.		S-29-82	S-29-82 dup.
Sample vol (ul)	1000	1000		1000	1000		1000	1000
Sample inject (ul)	10	10		2.5	2.5		4.5	4.5
Wet wt (gm)	5	5		5	5		10	10
Dry wt (mg)	3.250	3.248		3.016	3.016		5.420	5.420
Organic wt (mg)	115.361	90.915		263.417	263.417		177.180	117.180
No. of compounds	18	18		18	18		18	18
1 Fluorene	3.816	2.969		2.904	3.188		5.753	6.468
2 Phenanthrene	28.324	26.987		22.256	22.191		40.381	40.366
3 Anthracene	3.847	5.244		7.481	6.631		14.910	12.387
4 Fluoranthene	45.079	46.490		43.745	40.169		111.323	104.175
5 MePhenanth	6.065	5.986		4.032	3.977		14.350	12.716
6 Pyrene	23.258	22.979		27.709	25.608		71.438	62.502
7 MeAnthracene	2.102	1.364		2.008	2.422		9.755	9.644
8 Benzofluor	11.349	7.594		11.412	13.035		99.112	101.007
9 Benzanth	8.646	10.296		12.430	11.451		24.292	25.964
10 Chrysene	0	0		8.550	7.610		17.177	14.672
11 Benzo(e)pyr	8.002	8.082		10.680	8.029		85.420	87.160
12 Perylene	13.661	16.145		18.533	17.217		112.536	107.605
13 Benzo(b)fluor	8.389	13.352		9.494	8.768		33.380	34.080
14 Benzo(k)fluor	5.040	5.549		6.033	6.352		13.003	14.463
15 Benzo(a)pyr	6.141	7.093		10.896	10.436		23.670	26.622
16 Dibenz(a,h)anth	1.575	1.752		2.015	2.284		5.670	8.584
17 Benzo(g,h,i)peryl	5.358	6.434		7.338	7.427		29.959	40.246
18 Indeno(1,2,3-c,d)pyr	6.837	7.305		9.183	10.063		50.202	49.737

SEDIMENT RECOVERIES (ng/gm)

Sample name	S-16-82	S-16-82 dup.	S-16-82spike	%Recovery	S-29-82	S-29-82 dup.	S-29-82spike	%Recovery
Sample vol (ul)	1000	1000	1000		1000	1000	1000	
Sample inject (ul)	2.5	2.5	2.5		4.5	4.5	4.5	
Wet wt (gm)	5	5	5		10	10	10	
Dry wt (mg)	3.016	3.016	3.016		5.42	5.42	5.42	
Organic wt (mg)	263.417	263.417	263.417		177.18	177.18	177.18	
No. of compounds	18	18	18		18	18	18	
1 Fluorene	2.904	3.188	27.621	90.3	5.753	6.468	27.750	72.4
2 Phenanthrene	22.256	22.191	50.265	>100.0	40.381	40.366	46.864	60.6
3 Anthracene	7.481	6.631	33.227	95.2	14.910	12.387	38.958	90.6
4 Fluoranthene	43.745	40.169	74.412	>100.0	111.323	104.175	91.156	60.6
5 MePhenanth	4.032	3.977	32.095	>100.0	14.350	12.716	36.477	82.8
6 Pyrene	27.709	25.608	54.478	>100.0	71.438	62.502	69.074	89.9
7 MeAnthracene	2.008	2.422	27.877	98.7	9.755	9.644	33.563	86.8
8 Benzofluor	11.412	13.035	39.593	>100.0	99.112	101.007	90.661	74.4
9 Benzanth	12.430	11.451	36.607	91.6	24.292	25.964	36.011	59.6
10 Chrysene	8.550	7.610	32.288	94.7	17.177	14.672	35.715	81.8
11 Benzo(e)pyr	10.680	8.028	47.160	>100.0	85.420	87.160	50.161	0
12 Perylene	18.533	17.217	43.589	98.2	112.536	107.605	95.385	70.0
13 Benzo(b)fluor	9.494	8.768	9.723	-----	33.380	34.080	18.289	----
14 Benzo(k)fluor	6.033	6.352	6.746	-----	13.003	14.463	8.872	----
15 Benzo(a)pyr	10.896	10.436	29.271	82.2	23.670	26.622	38.858	81.3
16 Dibenz(a,h)anth	2.015	2.284	26.134	>100.0	5.670	8.584	28.872	85.0
17 Benzo(g,h,i)peryl	7.338	7.327	32.450	>100.0	29.959	40.246	46.776	93.3
18 Indeno(1,2,3-c,d)pyr	9.183	10.063	10.357	-----	50.202	49.737	13.637	----

(ng/liter) WATER RECOVERIES C_{18} Mini column

Sample name		Hoover Cr.	Hoover Cr. Dup.		% Recovery			
Sample vol (ul)		50	50					
Sample inject (ul)								
Wet wt (gm)								
Dry wt (mg)								
Organic wt (mg)								
No. of compounds								
1 Fluorene								
2 Phenanthrene								
3 Anthracene								
4 Fluoranthene		28.790	98.084		14.9			
5 MePhenanth								
6 Pyrene		12.640	75.064		4.8			
7 MeAnthracene								
8 Benzofluor								
9 Benzanth		0.868	48.295		26.2			
10 Chrysene		1.297	37.892		24.1			
11 Benzo(e)pyr								
12 Perylene								
13 Benzo(b)fluor								
14 Benzo(k)fluor								
15 Benzo(a)pyr		1.084	18.158		28.0			
16 Dibenz(a,h)anth		0.265	17.762		10.7			
17 Benzo(g,h,i)peryl		1.332	16.786		11.6			
18 Indeno(1,2,3-c,d)pyr								

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-905/4-85-002	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Investigation of Polycyclic Aromatic Hydrocarbon Discharges to Water in the Vicinity of Buffalo New York		5. REPORT DATE February 1985 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Edward J. Kuzia and John J. Black		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS New York State Department of Environmental Conservation 50 Wolf Road Albany, New York 12233		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. R00556610-01
12. SPONSORING AGENCY NAME AND ADDRESS U.S.Environmental Protection Agency Great Lakes National Program Office Chicago, Illinois 60605		13. TYPE OF REPORT AND PERIOD COVERED Final 14. SPONSORING AGENCY CODE Great Lakes National Program Office USEPA, Region V

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Eastern Lake Erie and the upper Niagara River basin were sampled for polycyclic aromatic hydrocarbons (PAH) to assess their distribution and sources. Twenty-five sites were sampled using polypropylene substrates. Five areas were identified as having relatively high PAH contamination. These were Lake Erie at the mouth of Smoke Creek, the Union and Lackawanna Ship Canals, the Buffalo River, Two Mile Creek, and the Buffalo Sewer Authority. Subsequent sampling and analyses of sediments, water, and polypropylene substrates confirmed the preliminary findings. The sources of the PAH were attributed to steel manufacturing operations (Lake Erie at the mouth of Smoke Creek and Union and Lackawanna Ship Canals) and oil storage facilities (Two Mile Creek). The Buffalo Sewer Authority was sampled directly in the outfall, and the analytical results identified it as a source of PAH to the Niagara River. The Buffalo River had several PAH inputs near the South Park Bridge. In addition to the areas identified as having high PAH contamination, there was a generalize PAH contamination throughout the study area.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Polycyclic Aromatic Hydrocarbons Contaminants Sediments Waters		

18. DISTRIBUTION STATEMENT Document is available to the public through the National Technical Information Service Springfield, Virginia 22151	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 144
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

☆ U.S. GOVERNMENT PRINTING OFFICE: 1985—555-755/549